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Quantum theory of van der Waals interactions between excited atoms and birefringent dielectric surfaces

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Abstract. A theory of van der Waals (vdW) interaction between an atom (in ground or excited state) and a birefringent dielectric surface with an arbitrary orientation of the principal optic axis (C-axis) is presented. Our theoretical approach is based on quantum-mechanical linear response theory, using generalized susceptibilities for both atom and electromagnetic field. Resonant atom-surface coupling is predicted for excited-state atoms interacting with a dispersive dielectric surface, when an atom de-excitation channel gets into resonance with a surface polariton mode. In the non-retarded regime, this resonant coupling can lead to enhanced attractive or repulsive vdW surface forces, as well as to a dissipative coupling increasing the excited-state relaxation. We show that the strongly non-scalar character of the interaction with the birefringent surface produces a C-axis-dependent symmetry-breaking of the atomic wavefunction. Changes of the C-axis orientation may also lead to a frequency shift of the surface polariton mode, allowing for tuning *on* or *off* the resonant coupling, resulting in a special type of engineering of surface forces. This is analysed here in the case of cesium $6D_{3/2}$ level interacting with a sapphire interface, where it is shown that an adequate choice of the sapphire C-axis orientation allows one to transform vdW surface attraction into repulsion, and to interpret recent experimental observations based on selective reflection methods [H. Failache *et al.*, Phys. Rev. Lett. **83**, 5467 (1999)].

PACS. 42.50.Ct Quantum description of interaction of light and matter; related experiments – 12.20.Ds Specific calculations – 32.70.Jz Line shapes, widths, and shifts

1 Introduction

Van der Waals forces between neutral polarisable bodies [1–6] represent an ubiquitous interaction, the influence of which is central in numerous fields of physics, chemistry and biology. In physical sciences, the van der Waals (vdW) interactions are responsible for collisional shifts and broadening of spectral lines in vapours, and their attractive character is essential for the cohesion of numerous molecular systems or clusters, among many other effects. Recently the long-range dipole attraction between atomic systems and metallic or dielectric bodies (Lennard-Jones [2]) has been the subject of a renewed interest because of its fundamental importance in the field of cavity Quantum Electrodynamics (QED) [7], or in atomic-force microscopes [8]. In this case, the vdW interaction originates in the quantum fluctuations of the atomic dipole which instantaneously polarises the surface, and induces a correlated dipole image. This near-field image is responsible for the attractive character of the vdW interaction, which scales in $1/d^3$ (d is the atom-surface distance) [2].

Many theoretical studies of vdW atom-surface interactions have been performed over the years, starting with ground-state atoms interacting with perfect metallic mirrors, both in the non-retarded and retarded regime (*e.g.* propagation effects [4]): level shifts, distance laws for surface forces... The influence of the material dispersion for metallic or dielectric surfaces has been analysed by several authors [9–12]. Also the effect of atomic excitation has been considered to describe enhancement or inhibition of spontaneous emission in a confined space, along with surface-induced level shifts, for either perfect reflectors [12–14] or ideal dielectric surfaces [15]. On the other hand, dielectric dispersion and the related surface polariton resonances have been included in several theoretical approaches to excited-state interactions [12,16–18]. Virtual energy exchange between excited atom and surface may lead to a resonant enhancement of the interaction, along with a possibility of sign reversal, *i.e.* the prediction of atom-surface van der Waals repulsion which has

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been recently observed in selective reflection spectroscopy experiments [19].

In all the above works, the solid-state medium is assumed to be homogeneous and isotropic. Interactions of ground state atoms with *birefringent* dielectrics has been studied by a few authors for an optic axis normal to the surface [20]. Extension to excited-state atoms has been performed for an optic axis normal to the surface [18]. For ground-state atoms, it has been shown by Fichet *et al.* [18] (*e.g.* in the case of a sapphire surface), that the birefringence of the dielectric medium does not basically modify the properties of the atom-surface interaction because ordinary and extraordinary indices are not very different in the wavelength range outside of the resonances. This is no longer the case for *excited-state* atoms interacting with *birefringent* dispersive dielectrics in the presence of a *resonant coupling* [18]: surface polariton resonances may strongly depend on the relative orientation of the crystal C-axis and the surface normal, inducing a surface polariton shift with the crystal orientation which may "tune" the atom-surface coupling on- and off-resonance.

The object of this article is to present a general theoretical description of the non-retarded interaction between an atom (in an *arbitrary* internal energy state) and a dispersive dielectric surface with an *arbitrary* orientation of the birefringence axis.

2 Theoretical framework

As recalled above, in the simple case of uniaxial media whose principal optic axis is perpendicular to the interface, the form of the interaction has been derived in [18]. In that case, the cylindrical symmetry of the system around the optic axis allows us to use the well-known image dipole model to derive an interaction scaling in d^{-3}, like in the isotropic case, but with an image factor:

$$\frac{\bar{\varepsilon}-1}{\bar{\varepsilon}+1}, \quad \text{where} \quad \bar{\varepsilon}=\sqrt{\varepsilon_e\varepsilon_0}. \tag{1}$$

In equation (1), ε_e, ε_0 are respectively the extraordinary and ordinary dielectric constants.

For an uniaxial crystal whose optic axis makes an angle θ with the normal to the surface, the problem is much more complicated, and we can no longer use the image model.

In the case of an atom at thermal equilibrium at 0 K, *i.e.* for an atom in its ground state, there have been many related works about the interaction between two macroscopic *anisotropic* media with flat parallel interfaces in thermal equilibrium at 0 K (see for example [21–23]). Then, diluting one of the media down to one atom, one can deduce the van der Waals shift of the atomic ground-state. This approach does not work for an arbitrary excited state, which cannot be described in a thermal equilibrium formalism.

So, to analyse the excited-state response, we generalize the quantum-mechanical linear-response formalism ([10–12]) to the case of an anisotropic dispersive dielectric interface, in order to derive the level-shifts of atoms in an arbitrary internal state. In Section 3, we remind the expression of the interaction Hamiltonian and the calculation of the shift for any *non-degenerate* state, as done in [12]. In Section 4, we consider the particular case of an interface with anisotropic media, whose optic axis makes an arbitrary angle θ with the normal to the surface. We derive also the modification of the transition rate of any excited state of the atom near an birefringent interface as well as the modification of all transition probabilities (Sect. 5). Then, it is possible to write (Sect. 6) the evolution equations for the atom due to the coupling with the reservoir (vacuum+surface). We define an effective Hamiltonian in Section 7. Knowing its off-diagonal elements, this allows us to give an example of application of this work to sapphire and cesium (Sect. 8), in relation with recent experiments [19,29].

The key-point of this work, after having developed the field radiated by the dipole in a sum of plane waves, is to derive the field reflected by the surface at the location of the dipole, and consequently to calculate the *Fresnel coefficients* for the reflection of a plane wave by an anisotropic interface. Starting with Maxwell equations and boundary conditions at the interface, it is a cumbersome work, while one only needs the limit of these coefficients in the non-retarded case. We can also find directly this limit using electrostatic equations with appropriate boundary conditions (Appendix A). We verify that we obtain the same result on the simple case of the optic axis perpendicular to the interface (Appendix B).

To conclude this introduction, we specify our basic assumptions:

- $d \ll \lambda$ where λ represents any wavelength corresponding to a transition between states of the atom or of the dielectric;
- $d \gg a_0$, where a_0 is the inter-atomic distance in the solid media. That allows us to describe it with macroscopic dielectric constants ε_0 and ε_e, whose values will appear in Fresnel coefficients;
- the atom is treated as a purely quantum-mechanical object, not necessarily isotropic.

3 Level-shift of an arbitrary atomic state

We keep only the dipolar term in the multipolar development of the interaction between the charges and the field (Power-Zienau-Woolley Hamiltonian: see for example [24] p. 282). What is called "the charges" is the fluctuating atomic dipole, located at a point $\mathbf{r}_0$ (see Fig. 1). What is called "the field", or "reservoir" is the rest of the system, supposed first without any interaction with the atom (radiation field in presence of the surface, but also surface excitations, etc.). We consider only the case of low temperatures: $kT \ll \hbar\omega$, where $\hbar\omega$ is the lowest typical energy among atomic or surface transition energies. Then, the coupling Hamiltonian is written:

$$V=-\int \mathbf{P}(\mathbf{r})\cdot\mathbf{D}(\mathbf{r})\mathrm{d}\mathbf{r} \tag{2}$$

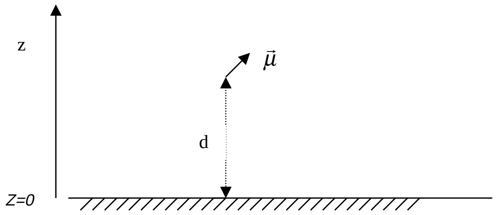

Fig. 1. Location of the atomic dipole above the interface.

$\mathbf{D}(\mathbf{r})$ is the displacement field operator, transverse for a neutral system. $\mathbf{P}(\mathbf{r})$ is the polarisation density operator. Here we have: $\mathbf{P}(\mathbf{r}) = \boldsymbol{\mu}\delta(\mathbf{r}-\mathbf{r}_0)$, $\boldsymbol{\mu}$ being the dipole moment operator. This gives for the Hamiltonian:

$$V = -\boldsymbol{\mu}\cdot\mathbf{D}(\mathbf{r}_0). \tag{3}$$

Then, following the linear response theory, the level-shifts can be expressed as functions of the susceptibilities of the field and of the atom in the $|a\rangle$ state. Keeping the notations of [12], we write them respectively $G_{\alpha\beta}(\mathbf{r},\mathbf{r}_0;\omega)$ and $\alpha^a_{\alpha\beta}(\omega)$. The Greek subscripts denote Cartesian components of the second order tensors $\overleftrightarrow{\mathbf{G}}$ and $\overleftrightarrow{\boldsymbol{\alpha}}^a$. They have to be summed over when repeated.

In quantum mechanics, the susceptibilities are defined from the correlation functions:
for the "field":

$$G_{\alpha\beta}(\mathbf{r},\mathbf{r}_0;t) = \frac{\mathrm{i}}{\hbar}\left\langle [D_\alpha(\mathbf{r},t), D_\beta(\mathbf{r}_0,0)]\right\rangle \Theta(t), \tag{4}$$

for the atom in a-state:

$$\alpha^a_{\alpha\beta}(t) = \frac{\mathrm{i}}{\hbar}\langle a|\,[\mu_\alpha(t),\mu_\beta(0)]\,|a\rangle\Theta(t). \tag{5}$$

In those formulas, $\mathbf{D}(\mathbf{r},t)$ and $\boldsymbol{\mu}(t)$ are now interaction-picture operators, and the angular brackets indicate: for $\overleftrightarrow{\mathbf{G}}$, an ensemble average (with Gibbs distribution) over the field-states, and, for $\overleftrightarrow{\boldsymbol{\alpha}}^a$, the mean value in the a-state of the atom. Normal brackets are usual commutators.

Taking the time Fourier transforms:

$$G_{\alpha\beta}(\mathbf{r},\mathbf{r}_0;\omega) = \int_{-\infty}^{+\infty} \mathrm{d}t\, G_{\alpha\beta}(\mathbf{r},\mathbf{r}_0;t)\mathrm{e}^{\mathrm{i}\omega t} \tag{6}$$

$$\alpha^a_{\alpha\beta}(\omega) = \int_{-\infty}^{+\infty} \mathrm{d}t\, \alpha^a_{\alpha\beta}(t)\mathrm{e}^{\mathrm{i}\omega t} \tag{7}$$

one obtains the susceptibilities we need.

In particular, the polarisability of an arbitrary a-state can be written:

$$\begin{aligned}\alpha^a_{\alpha\beta}(\omega) &= \frac{1}{\hbar}\sum_n\left[\frac{\mu^{an}_\alpha\mu^{na}_\beta}{\omega_{na}-(\omega+\mathrm{i}\eta)} + \frac{\mu^{na}_\alpha\mu^{an}_\beta}{\omega_{na}+(\omega+\mathrm{i}\eta)}\right]\\ &= \frac{2}{\hbar}\sum_n\frac{\omega_{na}\mu^{an}_\alpha\mu^{na}_\beta}{\omega^2_{na}-(\omega+\mathrm{i}\eta)^2},\end{aligned} \tag{8}$$

where $\mu^{na}_\alpha = \langle n|\mu_\alpha|a\rangle = \mu^{an}_\alpha$ is assumed (for the free atom, with time-reversal invariance, wave-functions of states a and n can be chosen real), and $\eta \to 0+$.

For the field, the simplest way to have the susceptibility at frequency ω is to remember, from linear-response theory, that $\overleftrightarrow{\mathbf{G}}(\mathbf{r},\mathbf{r}_0;\omega)\boldsymbol{\mu}$ is the expectation value of the displacement field at $\mathbf{r}$ generated by a classical dipole oscillating at frequency ω: $\boldsymbol{\mu}(t) = \boldsymbol{\mu}_0\mathrm{e}^{-\mathrm{i}\omega t}$, located at $\mathbf{r}_0$ (see [24], p. 354, ex. 6).

In the half-space above the interface, where is located the atom, the relation between the electric field and the displacement field is then:

$$\mathbf{D}(\mathbf{r},t) = \mathbf{E}(\mathbf{r},t) + 4\pi\boldsymbol{\mu}(t)\delta(\mathbf{r}-\mathbf{r}_0). \tag{9}$$

For the component oscillating at ω, the tensorial Green functions of the dipole are denoted: $\overleftrightarrow{\mathbf{F}}(\mathbf{r},\mathbf{r}_0;\omega)$ for the electric field and $\overleftrightarrow{\mathbf{G}}(\mathbf{r},\mathbf{r}_0;\omega)$ for the displacement field:

$$\begin{aligned}\mathbf{E}(\mathbf{r},\omega) &= \overleftrightarrow{\mathbf{F}}(\mathbf{r},\mathbf{r}_0;\omega)\boldsymbol{\mu},\\ \mathbf{D}(\mathbf{r},\omega) &= \overleftrightarrow{\mathbf{G}}(\mathbf{r},\mathbf{r}_0;\omega)\boldsymbol{\mu}.\end{aligned} \tag{10}$$

We have: $G_{\alpha\beta} = G^{\mathrm{R}}_{\alpha\beta} + G^0_{\alpha\beta}$, $G^0_{\alpha\beta}$ being the vacuum susceptibility (that of the field radiated by an atom in free space), and $G^{\mathrm{R}}_{\alpha\beta}$ the susceptibility of the field reflected by the surface. Using equations (9, 10):

$$\begin{aligned}G^0_{\alpha\beta}(\mathbf{r},\mathbf{r}_0;\omega) &= F^0_{\alpha\beta}(\mathbf{r},\mathbf{r}_0;\omega) + 4\pi\delta_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}_0),\\ G^{\mathrm{R}}_{\alpha\beta}(\mathbf{r},\mathbf{r}_0;\omega) &= F^{\mathrm{R}}_{\alpha\beta}(\mathbf{r},\mathbf{r}_0;\omega).\end{aligned} \tag{11}$$

(It is the last function that we need to obtain the contribution of the anisotropic interface.)

Using second-order perturbation, the calculation leads to the *total* shift (vacuum + surface) of an arbitrary atomic state $|a\rangle$:

$$\begin{aligned}\delta E_a = \mathrm{P}\sum_{I,N,n} p(I)\langle a,I|V|n,N\rangle\langle n,N|V|a,I\rangle\\ \times\left[\frac{1}{E_I+E_a-E_N-E_n}\right],\end{aligned} \tag{12}$$

where P denotes the principal part. Capital letters indicate eigenstates of the reservoir, small letters those of the atom, when there is no interaction between them.

The *surface contribution* appears as the sum of two terms: δE^{fl}_a, which is the part of the shift due to quantum-mechanical fluctuations, and $\delta E^{\mathrm{res}}_a$, its resonant part, which exists only for excited states of the atom, and has a classical analogy:

$$(\delta E_a)^{\mathrm{surf}} = \delta E^{\mathrm{fl}}_a + \delta E^{\mathrm{res}}_a, \tag{13a}$$

$$\begin{aligned}\delta E^{\mathrm{fl}}_a &= -\frac{1}{\pi}\sum_n\omega_{na}\mu^{an}_\alpha\mu^{na}_\beta\int_0^\infty \mathrm{d}\xi\frac{G^{\mathrm{R}}_{\alpha\beta}(\mathbf{r}_0,\mathbf{r}_0;\mathrm{i}\xi)}{\xi^2+\omega^2_{na}}\\ &= -\frac{\hbar}{2\pi}\int_0^\infty \mathrm{d}\xi\, G^{\mathrm{R}}_{\alpha\beta}(\mathbf{r}_0,\mathbf{r}_0;\mathrm{i}\xi)\alpha_{\alpha\beta}(\mathrm{i}\xi),\end{aligned} \tag{13b}$$

$$\delta E^{\mathrm{res}}_a = -\sum_n\mu^{an}_\alpha\mu^{na}_\beta\mathrm{Re}G^{\mathrm{R}}_{\alpha\beta}(\mathbf{r}_0,\mathbf{r}_0;\omega_{na})\Theta(\omega_{an}). \tag{13c}$$

In formulas (13): $\Theta(\omega_{an})$ is the Heaviside function, and $\omega_{na} = \omega_n - \omega_a$ must be negative to give a non-zero value

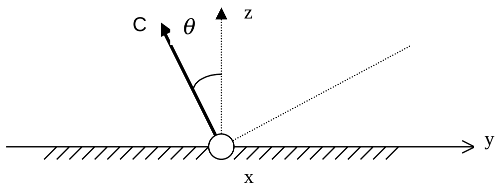

Fig. 2. The x-axis is the intersection of the interface plane with the plane perpendicular to the principal optic axis C. The angle between this optic axis and the normal to the surface (z-axis) is θ.

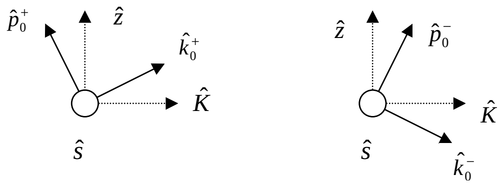

Fig. 3. Unit vectors for propagating waves in the vacuum (index 0). $\hat{\mathbf{s}}$ and $\hat{\mathbf{K}}$ are in the interface plane, and normal to each other. $\hat{\mathbf{k}}_0^-$ is the incident wave-vector, $\hat{\mathbf{k}}_0^+$ is the reflected one.

to the second term. $G^{\mathrm{R}}_{\alpha\beta}(\mathbf{r},\mathbf{r}_0;\omega)$ and $\alpha^a_{\alpha\beta}(\omega)$ are functions of the complex variable ω, analytic in the upper half-plane and taking purely real values for imaginary frequencies (iξ).

Now, we have to find the contribution of the reflected field to the susceptibility, *in the case of an anisotropic interface with an arbitrary oriented optic axis.*

4 Level-shift of an atom near an anisotropic surface

4.1 Introduction

We generalize the work of Sipe [25] to the case of an anisotropic interface, writing the susceptibility of the field reflected by the surface at the position of the atom:

$$\overleftrightarrow{\mathbf{G}}^{\mathrm{R}}(\mathbf{r}_0,\mathbf{r}_0;\omega) = \frac{\mathrm{i}k_0^2}{2\pi}\int \frac{\mathrm{d}\mathbf{K}}{W_0}\left(R^{ss}\hat{\mathbf{s}}\hat{\mathbf{s}} + R^{sp}\hat{\mathbf{s}}\hat{\mathbf{p}}_0^- + R^{ps}\hat{\mathbf{p}}_0^+\hat{\mathbf{s}} + R^{pp}\hat{\mathbf{p}}_0^+\hat{\mathbf{p}}_0^-\right)\mathrm{e}^{\mathrm{i}(2W_0 d)}. \quad (14)$$

In the isotropic case, an incident s-wave is reflected into a s-wave, and an incident p-wave into a p-one. For reflection of a wave coming from an isotropic media (vacuum here) upon an anisotropic interface, we must calculate the four Fresnel coefficients R^{ij} to obtain the s and p components of the reflected field in function of the s and p components of the incident one:

$$\begin{aligned} E_s^{\mathrm{R}} &= R^{ss}E_s^{\mathrm{I}} + R^{sp}E_p^{\mathrm{I}}, \\ E_p^{\mathrm{R}} &= R^{ps}E_s^{\mathrm{I}} + R^{pp}E_p^{\mathrm{I}}. \end{aligned} \quad (15)$$

Let us first explain the notations used in equation (14): see Figures 1–3.

In Cartesian coordinates, with unit vectors denoted: $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$, the dielectric surface is the ($\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$) plane, and the location of the atom is: $\mathbf{r}_0 = x_0\hat{\mathbf{x}} + y_0\hat{\mathbf{y}} + d\hat{\mathbf{z}}$, where d is positive. The x-axis is chosen parallel to the intersection of any plane perpendicular to the optic axis with the plane of the interface, and the $\hat{\mathbf{x}}$-direction can always be chosen in such a way that the azimuthal angle φ between $\hat{\mathbf{x}}$ and $\mathbf{K}$ satisfies $(\varepsilon_0 - \varepsilon_e)\sin\varphi > 0$, $\mathbf{K}$ being the projection of the wave-vector on the ($\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$) plane. This condition is necessary for getting a physical solution to Maxwell equations into the dielectric (see Appendix A).

Formula (14) yields the reflected field as a superposition of plane waves with real wave-vector components ($K\cos\varphi\hat{\mathbf{x}}$, $K\sin\varphi\hat{\mathbf{y}}$) in the plane of the interface. In the z-direction, the waves are propagating or evanescent depending whether $K < k_0$ or $K > k_0 = \omega/c$. Then, the wave-vectors in the vacuum are written: $\mathbf{k}_0^{\pm} = \mathbf{K} \pm W_0\hat{\mathbf{z}}$, in which subscript 0 in W_0 indicates that the propagation takes place in the vacuum. The complex root $W_0 = \left(k_0^2 - K^2\right)^{1/2}$ must have either $\mathrm{Re}W_0 > 0$ when $\mathrm{Im}W_0 = 0$, or $\mathrm{Im}W_0 > 0$ when $\mathrm{Re}W_0 = 0$.

The unit vectors $\hat{\mathbf{s}}$ and $\hat{\mathbf{p}}_0^{\pm}$ specify the directions of the electric vector in s and p polarised waves (see Fig. 3):

$$\begin{aligned} \hat{\mathbf{s}} &= \hat{\mathbf{K}} \times \hat{\mathbf{z}} \\ \hat{\mathbf{p}}_0^{\pm} &= k_0^{-1}(\mp W_0\hat{\mathbf{K}} + K\hat{\mathbf{z}}), \end{aligned} \quad (16)$$

where $\hat{\mathbf{K}} = \mathbf{K}/K$.

In the case of p-polarisation, these vectors are different for reflected (+) or incident (−) propagating or evanescent waves, which makes appear the term $\hat{\mathbf{p}}_0^+\hat{\mathbf{p}}_0^-$. The notations like $\hat{\mathbf{p}}_0^+\hat{\mathbf{p}}_0^-$ indicates a projector; for example, $(\hat{\mathbf{p}}_0^+\hat{\mathbf{p}}_0^-)\boldsymbol{\mu} = \hat{\mathbf{p}}_0^+(\hat{\mathbf{p}}_0^- \cdot \boldsymbol{\mu})$. A phase-vector $\mathrm{e}^{2\mathrm{i}W_0 d}$ also appears because of the reflection from the surface.

With these notations, we can specify that, in equation (15): $E_p^{\mathrm{R}} = E_{p_0^+}$ and $E_p^{\mathrm{I}} = E_{p_0^-}$.

Then, to obtain the ω-component of the field reflected by the surface at the location of the atom: $\mathbf{E}^{\mathrm{R}}(\mathbf{r}_0,\omega) = \overleftrightarrow{\mathbf{G}}^{\mathrm{R}}(\mathbf{r}_0,\mathbf{r}_0;\omega)\boldsymbol{\mu}$, we have to calculate the four Fresnel coefficients *in the retarded regime.* For that, one has to write the boundary conditions at the interface: continuity of tangential components of $\mathbf{E}$ and $\mathbf{B}$ and continuity of the normal component of $\mathbf{D}$, the fields being a sum of an incident field and a reflected one in the vacuum, and a sum of an ordinary field and an extraordinary one in the birefringent dielectric. This leads to a linear system of six equations for each component (s and p) of the incident wave. The solution for any value of the angle θ between the optic axis and the normal to the interface cannot take a simple form. In Appendix B, we calculate the values of retarded Fresnel coefficients for the simplest case $C_{\perp}(\theta = 0)$. For an arbitrary angle, the calculation is much too cumbersome and we will see below that we do not need it really.

4.2 Near-field limit

Here, we look for the *near-field limit* of the van der Waals shift, when the location of the atom and all characteristic frequencies of the atom ω_i and of the dielectric ω_j are such that $\omega_{i,j}/c \ll 1/d$. So we only need the *quasi-stationary limit* of $\overleftrightarrow{\mathbf{G}}^{\mathrm{R}}$.

First, we can note that, among the sum of operators contributing to $\overleftrightarrow{\mathbf{G}}^{\mathrm{R}}$ in formula (14), only $k_0^2\hat{\mathbf{p}}_{0+}\hat{\mathbf{p}}_{0-}$ is not vanishing when $k_0 = \omega/c \to 0$ (see the expression of unit vectors $\hat{\mathbf{s}}$ and $\hat{\mathbf{p}}$ in Eq. (16)).

Secondly, we see in Appendix A that only R^{pp} has a non-zero static limit, and keeps the meaning of a "*reflection*" coefficient on a dispersive dielectric surface for static fields[1].

So we calculate the $k_0 = \omega/c \to 0$ limit of R^{pp} for any angle θ $(0 \leq \theta \leq \pi/2)$ between the optic axis of the uniaxial medium and the normal to the surface, writing the boundary conditions directly in the electrostatic regime. The calculation is reported in Appendix A. We find:

$$R_\theta^{\mathrm{st}}(\varphi) = \frac{\sqrt{\varepsilon_0\varepsilon_e\left(1+\delta\sin^2\theta\cos^2\varphi\right)}-1}{\sqrt{\varepsilon_0\varepsilon_e\left(1+\delta\sin^2\theta\cos^2\varphi\right)}+1}\cdot \tag{17}$$

In this formula, $\delta = (\varepsilon_0 - \varepsilon_e)/\varepsilon_e$.

Of course, in formulas (13) giving the van der Waals shift, this zero-order limit in ω/c must remain valid when performing the integration over frequencies. We must remind that $\alpha^a_{\alpha\beta}(\omega)$ takes significant values only in narrow domains around some frequencies ω_i. In these domains, under the condition: $\omega_i/c \ll 1/d$, we can take the quasi-static limit of R^{pp} (we call it R^{st}) to calculate $G^{\mathrm{R}}_{\alpha\beta}(\mathbf{r}_0,\mathbf{r}_0;\omega\approx 0)$. But we have to take into account the dependence of the Fresnel coefficient on ω, through the dependence of the dielectric constants ε_0 and ε_e of the dispersive media: like $\alpha^a_{\alpha\beta}(\omega)$, ε_0 and ε_e are functions of ω smooth everywhere except around some frequencies ω_j such that: $\omega_j/c \ll 1/d$.

Finally, to calculate the near-field limit of $\overleftrightarrow{\mathbf{G}}^{\mathrm{R}}(\mathbf{r}_0,\mathbf{r}_0;\omega)$, we assume in equation (14): $R^{pp} \approx R_\theta^{\mathrm{st}}(\varphi,\omega)$, where the ω-dependence of R^{pp} comes now only from the dependency of ε_e and ε_0 on ω. We said above that, among the sum of operators contributing to $\overleftrightarrow{\mathbf{G}}^{\mathrm{R}}$, only $k_0^2\hat{\mathbf{p}}_0^+\hat{\mathbf{p}}_0^-$ is not vanishing when $k_0 = \omega/c \to 0$. So, we have simply, using equation (16) and integrating over K:

$$\overleftrightarrow{\mathbf{G}}^{\mathrm{R}}_{\mathrm{st}}(\mathbf{r}_0,\mathbf{r}_0;\omega) = \frac{1}{8\pi d^3}\int_0^{2\pi} \mathrm{d}\varphi\, R_\theta^{\mathrm{st}}(\varphi,\omega)\,\overleftrightarrow{\mathbf{P}}(\varphi) \tag{18}$$

with:

$$\overleftrightarrow{\mathbf{P}}(\varphi) = \begin{pmatrix} \cos^2\varphi & \sin\varphi\cos\varphi & -\mathrm{i}\cos\varphi \\ \sin\varphi\cos\varphi & \sin^2\varphi & -\mathrm{i}\sin\varphi \\ \mathrm{i}\cos\varphi & \mathrm{i}\sin\varphi & 1 \end{pmatrix}\cdot \tag{19}$$

Then, this solution reported in equation (13) leads to the following expression for the quantum-mechanical level-shift:

$$\delta E_a^{\mathrm{fl}}(\theta) = -\frac{1}{16d^3}\sum_n A_\theta(\omega_{na})\left|\mu_x^{an}\right|^2 + B_\theta(\omega_{na})\left|\mu_y^{an}\right|^2 + \left[A_\theta(\omega_{na}) + B_\theta(\omega_{na})\right]\left|\mu_z^{an}\right|^2 \tag{20}$$

with:

$$A_\theta(\omega_{na}) = \frac{2}{\pi}\int_0^\infty \mathrm{d}\xi \frac{\omega_{na}}{\omega_{na}^2+\xi^2}\int_0^{2\pi}\frac{\mathrm{d}\varphi}{\pi}\left[R_\theta^{\mathrm{st}}(\varphi,\mathrm{i}\xi)\right]\cos^2\varphi \tag{21a}$$

$$B_\theta(\omega_{na}) = \frac{2}{\pi}\int_0^\infty \mathrm{d}\xi \frac{\omega_{na}}{\omega_{na}^2+\xi^2}\int_0^{2\pi}\frac{\mathrm{d}\varphi}{\pi}\left[R_\theta^{\mathrm{st}}(\varphi,\mathrm{i}\xi)\right]\sin^2\varphi \tag{21b}$$

(the sum is over all atomic-state n coupled by dipolar transition to the a-state. In general, n must include all the quantum numbers which define the n-state), and its resonant part, which can be written:

$$\delta E_a^{\mathrm{res}}(\theta) = -\frac{1}{16d^3}\sum_{n<a} A'_\theta(\omega_{na})\left|\mu_x^{an}\right|^2 + B'_\theta(\omega_{na})\left|\mu_y^{an}\right|^2 + \left[A'_\theta(\omega_{na}) + B'_\theta(\omega_{na})\right]\left|\mu_z^{an}\right|^2 \tag{22}$$

with:

$$A'_\theta(\omega_{na}) = \int_0^{2\pi}\frac{\mathrm{d}\varphi}{\pi}2\left[\mathrm{Re}R_\theta^{\mathrm{st}}(\varphi,\omega_{na})\right]\cos^2\varphi \tag{23a}$$

$$B'_\theta(\omega_{na}) = \int_0^{2\pi}\frac{\mathrm{d}\varphi}{\pi}2\left[\mathrm{Re}R_\theta^{\mathrm{st}}(\varphi,\omega_{na})\right]\sin^2\varphi. \tag{23b}$$

For the resonant part, the notation $n < a$ indicates that the sum is only over all n-states such that $\omega_n < \omega_a$ (coupling in emission).

In the case of cylindrical symmetry (axis normal to the surface, $\theta = 0$), R_θ^{st} depends no longer on φ and we recover the same results as in reference [18].

4.3 VdW shift operator for a non-degenerate level a

For the contribution of the anisotropic (or isotropic) surface to the shift, we can write (see Eqs. (13, 20, 22)):

$$\delta E_a^{\mathrm{surf}} = \langle a|W(a)|a\rangle, \tag{24}$$

where we have defined an operator $W(a)$ (vdW shift operator for level a) by:

$$W(a) = -\frac{1}{\pi}\sum_n(\mu_\alpha|n\rangle\langle n|\mu_\beta)\omega_{na}\int_0^{+\infty}\mathrm{d}\xi\frac{G^{\mathrm{R}}_{\alpha\beta}(\mathbf{r}_0,\mathbf{r}_0;\mathrm{i}\xi)}{(\xi^2+\omega_{na}^2)} - \sum_n(\mu_\alpha|n\rangle\langle n|\mu_\beta)\mathrm{Re}G^{\mathrm{R}}_{\alpha\beta}(\mathbf{r}_0,\mathbf{r}_0;\omega_{na})\Theta(\omega_{an}) \tag{25}$$

---

[1] We have to make an exception for the perfect conductor. The two Fresnel coefficients do not depend on ω. $R^{ss} = -1$, as well as: $R^{pp} = +1$, do not vanish in the static limit. In this case, it is the first argument which explains why we keep only the term in R^{pp} in the integrand of equation (14).

or, equivalently,

$$W(a)=\sum_n\left[-\frac{1}{\pi}\int_0^{+\infty}\mathrm{d}\xi\frac{\omega_{na}G^{\mathrm{R}}_{\alpha\beta}(\mathbf{r}_0,\mathbf{r}_0;\mathrm{i}\xi)}{(\xi^2+\omega_{na}^2)}\right.$$
$$\left.-\,\mathrm{Re}G^{\mathrm{R}}_{\alpha\beta}(\mathbf{r}_0,\mathbf{r}_0;\omega_{na})\Theta(\omega_{an})\right]\mu_\alpha|n\rangle\langle n|\mu_\beta. \quad (26)$$

Let us write:

$$\left[-\frac{1}{\pi}\int_0^{+\infty}\mathrm{d}\xi\frac{\omega_{na}G^{\mathrm{R}}_{\alpha\beta}(\mathbf{r}_0,\mathbf{r}_0;\mathrm{i}\xi)}{(\xi^2+\omega_{na}^2)}\right.$$
$$\left.-\,\mathrm{Re}G^{\mathrm{R}}_{\alpha\beta}(\mathbf{r}_0,\mathbf{r}_0;\omega_{na})\Theta(\omega_{an})\right]=C_{\alpha\beta}(a,n), \quad (27)$$

($C_{\alpha\beta}$ are real numbers). Then:

$$W(a)=\sum_n C_{\alpha\beta}(a,n)\mu_\alpha|n\rangle\langle n|\mu_\beta. \quad (28)$$

This is the general formula, valid for both retarded and static cases, and for any interface (isotropic, anisotropic, or perfect conductor). In the case of a birefringent uniaxe media, and within the near-field limit, we have found the simple formulas:

$$W(a)=W^{\mathrm{fl}}(a)+W^{\mathrm{res}}(a) \quad (29)$$
$$W^{\mathrm{fl}}(a)=-\frac{1}{16d^3}\sum_n A_\theta(\omega_{na})\mu_x|n\rangle\langle n|\mu_x$$
$$+B_\theta(\omega_{na})\mu_y|n\rangle\langle n|\mu_y$$
$$+(A_\theta(\omega_{na})+B_\theta(\omega_{na}))\mu_z|n\rangle\langle n|\mu_z \quad (30)$$
$$W^{\mathrm{res}}(a)=-\frac{1}{16d^3}\sum_n A'_\theta(\omega_{na})\mu_x|n\rangle\langle n|\mu_x$$
$$+B'_\theta(\omega_{na})\mu_y|n\rangle\langle n|\mu_y$$
$$+(A'_\theta(\omega_{na})+B'_\theta(\omega_{na}))\mu_z|n\rangle\langle n|\mu_z, \quad (31)$$

where the A, B, A', B' are defined in equations (21, 23).

5 Interface contribution to the transition rate in the case of birefringent media

In the same way, we can derive from equations (16–18) the modification of the transition rate of any excited atomic state induced by the reflected field. From Fermi's Golden rule, one finds (see [12]):

$$\Gamma^{\mathrm{surf}}_a=-\frac{2}{\hbar}\sum_n\mu^{an}_\alpha\mu^{na}_\beta\mathrm{Im}G^{\mathrm{R}}_{\alpha\beta}(\mathbf{r}_0,\mathbf{r}_0;\omega_{na})\Theta(\omega_{an})$$
$$=\sum_n\Gamma^{\mathrm{surf}}_{a\to n}. \quad (32)$$

Note that: $G_{\alpha\beta}(\mathbf{r},\mathbf{r}';-\omega)=G^*_{\alpha\beta}(\mathbf{r},\mathbf{r}';\omega)$. So, we can define a *positive* probability by second for the atom to do a transition from level a to level n because of the coupling with the reflected field, valid for any pair (a,n):

$$\Gamma^{\mathrm{surf}}_{a\to n}=\frac{2}{\hbar}\mu^{an}_\alpha\mu^{na}_\beta\mathrm{Im}G^{\mathrm{R}}_{\alpha\beta}(\mathbf{r}_0,\mathbf{r}_0;\omega_{an})\Theta(\omega_{an}). \quad (33)$$

Introducing two functions analogue to (21a, 21b) and (24a, 24b):

$$A''_\theta(\omega_{an})=\int_0^{2\pi}\frac{\mathrm{d}\varphi}{\pi}\left[\mathrm{Im}R^{\mathrm{stat}}_\theta(\varphi,\omega_{an})\right]\cos^2\varphi \quad (34a)$$
$$B''_\theta(\omega_{an})=\int_0^{2\pi}\frac{\mathrm{d}\varphi}{\pi}\left[\mathrm{Im}R^{\mathrm{stat}}_\theta(\varphi,\omega_{an})\right]\sin^2\varphi \quad (34b)$$

we obtain[2]:

$$\Gamma^{\mathrm{surf}}_{a,\theta}=\frac{2}{\hbar}\frac{1}{8d^3}\sum_{n<a}A''_\theta(\omega_{an})|\mu^{an}_x|^2+B''_\theta(\omega_{an})|\mu^{an}_y|^2$$
$$+\left[A''_\theta(\omega_{an})+B''_\theta(\omega_{an})\right]|\mu^{an}_z|^2. \quad (35)$$

In (35), *the sum is only over all n-state such that* $\omega_n<\omega_a$.

We can also define an operator $\Gamma^{\mathrm{surf}}(a)$ giving the modification of the width of level a by the surface:

$$\Gamma^{\mathrm{surf}}_a=\langle a|\frac{2}{\hbar}\sum_n(\mu_\alpha|n\rangle\langle n|\mu_\beta)\mathrm{Im}G^{\mathrm{R}}_{\alpha\beta}(\mathbf{r}_0,\mathbf{r}_0;\omega_{an})\Theta(\omega_{an})|a\rangle$$
$$=\langle a|\Gamma^{\mathrm{surf}}(a)|a\rangle \quad (36)$$

which gives in the anisotropic case:

$$\Gamma^{\mathrm{surf}}(a)=\frac{2}{\hbar}\frac{1}{8d^3}\sum_{n<a}A''_\theta(\omega_{an})(\mu_x|n\rangle\langle n|\mu_x)$$
$$+B''_\theta(\omega_{an})(\mu_y|n\rangle\langle n|\mu_y)$$
$$+\left[A''_\theta(\omega_{an})+B''_\theta(\omega_{an})\right](\mu_z|n\rangle\langle n|\mu_z). \quad (37)$$

6 Interface contribution to the atom master equation

With the help of equations (24–28) and (33–37), we can write the equations describing the evolution of populations and coherences under the coupling with the reservoir. *We write only the contribution of the surface to the master equation.* So, we keep only the contribution of the reflected field G^{R} to the linear susceptibility: $G=G^0+G^{\mathrm{R}}$, the other part giving the contribution of vacuum fluctuations without any surface. The vacuum contribution is given in [26] and references therein.

---

[2] As in Section 4, we have to treat separately the well-known case of the perfect conductor. Fresnel coefficients have no imaginary parts, and formulas (34, 35) are not correct. One has to look for the first non-zero term of $\mathrm{Im}G^{\mathrm{R}}_{\alpha\beta}$ when $\omega/c\to 0$ and apply (33). We recall that, for a perfect conductor, integration in equation (13) can be performed exactly, giving shifts, transition probabilities, and widths, *even in the retarded case* [12].

6.1 Evolution of populations due to the surface

In the secular approximation [26]:

$$\left(\frac{\mathrm{d}\sigma_{aa}}{\mathrm{d}t}\right)^{\mathrm{surf}} = \sum_{n\neq a}\left(\sigma_{nn}\Gamma^{\mathrm{surf}}_{n\to a} - \sigma_{aa}\Gamma^{\mathrm{surf}}_{a\to n}\right) = -\Gamma^{\mathrm{surf}}_{a}\sigma_{aa} + \sum_{n\neq a}\sigma_{nn}\Gamma^{\mathrm{surf}}_{n\to a} \qquad (38)$$

with $\Gamma^{\mathrm{surf}}_{a\to n} = (2/\hbar)\mu^{an}_{\alpha}\mu^{na}_{\beta}\mathrm{Im}G^{\mathrm{R}}_{\alpha\beta}(\mathbf{r}_0,\mathbf{r}_0;\omega_{an})\Theta(\omega_{an})$ (see Eqs. (33–35)), and $\omega_{an} = \omega_a - \omega_n$.

The modification of the width of level a being (see Eqs. (32, 36, 37)):

$$\Gamma^{\mathrm{surf}}_{a} = \sum_{n\neq a}\Gamma^{\mathrm{surf}}_{a\to n} = \sum_{n}\frac{2}{\hbar}\mu^{an}_{\alpha}\mu^{na}_{\beta}\mathrm{Im}G^{\mathrm{R}}_{\alpha\beta}(\mathbf{r}_0,\mathbf{r}_0;\omega_{an})\Theta(\omega_{an}) = \langle a|\Gamma^{\mathrm{surf}}(a)|a\rangle.$$

The last term of equation (38) gives, with equations (33–35) the part of population transferred from upper levels n to level a because of the surface.

6.2 Evolution of atomic coherences due to the surface

For a non-degenerate Bohr frequency ω_{ab}, in the secular approximation, the evolution under the total coupling is given by [26]:

$$\frac{\mathrm{d}\sigma_{ab}}{\mathrm{d}t} = \left(-\mathrm{i}\omega_{ab} - \mathrm{i}\Delta_{ab} - \Gamma_{ab}\right)\sigma_{ab}. \qquad (39)$$

The contribution of the surface appears in the last two terms.

(i) In $\Delta_{ab} = (1/\hbar)(\delta E_a - \delta E_b)$, we keep only the contribution of the reflected field to the shifts:

$$(\delta E_a - \delta E_b)^{\mathrm{surf}} = \langle a|W(a)|a\rangle - \langle b|W(b)|b\rangle, \qquad (40)$$

where $W(a)$ is defined in equations (24–31).

(ii) In:

$$\Gamma_{ab} = \frac{1}{2}\left(\sum_{n\neq a}\Gamma_{a\to n} + \sum_{n\neq b}\Gamma_{b\to n}\right) = \frac{1}{2}\left(\Gamma_a + \Gamma_b\right) \qquad (41)$$

we take also the contribution of the surface: $\Gamma^{\mathrm{surf}}_{ab} = (\Gamma^{\mathrm{surf}}_{a} + \Gamma^{\mathrm{surf}}_{b})/2$, where the Γ^{surf} are defined in equation (32).

Finally, the contribution of the reflected field to the evolution of coherences is:

$$\left(\frac{\mathrm{d}\sigma_{ab}}{\mathrm{d}t}\right)^{\mathrm{surf}} = \left(-\mathrm{i}\Delta_{ab} - \Gamma_{ab}\right)^{\mathrm{surf}}\sigma_{ab} \qquad (42)$$

$$= -\frac{\mathrm{i}}{\hbar}\left[\langle a|W(a)|a\rangle - \langle b|W(b)|b\rangle - \frac{\mathrm{i}\hbar}{2}\langle a|\Gamma^{\mathrm{surf}}(a)|a\rangle - \frac{\mathrm{i}\hbar}{2}\langle b|\Gamma^{\mathrm{surf}}(b)|b\rangle\right]\sigma_{ab}$$

$$= -\frac{\mathrm{i}}{\hbar}\left[\langle a|W(a) - \frac{\mathrm{i}\hbar}{2}\Gamma^{\mathrm{surf}}(a)|a\rangle - \langle b|W(b) + \frac{\mathrm{i}\hbar}{2}\Gamma^{\mathrm{surf}}(b)|b\rangle\right]\sigma_{ab}. \qquad (43)$$

If we define a non-Hermitian operator acting only on level a: $W'(a) = W(a) - (\mathrm{i}\hbar/2)\Gamma^{\mathrm{surf}}(a)$, equation (43) becomes:

$$\left(\frac{\mathrm{d}\sigma_{ab}}{\mathrm{d}t}\right)^{\mathrm{surf}} = -\frac{\mathrm{i}}{\hbar}\left[\langle a|W'(a)|a\rangle - \langle b|W'^{+}(b)|b\rangle\right]\sigma_{ab}. \qquad (44)$$

It is possible to introduce a purely diagonal non-Hermitian Hamiltonian:

$$W' = \sum_{i}|i\rangle\langle i|\,W'(i)|i\rangle\langle i|. \qquad (45)$$

Then, equation (44) gives:

$$\left(\frac{\mathrm{d}\sigma_{ab}}{\mathrm{d}t}\right)^{\mathrm{surf}} = -\frac{\mathrm{i}}{\hbar}\left[\left\langle a\left|W'\sigma - \sigma W'^{+}\right|b\right\rangle\right]. \qquad (46)$$

The diagonal elements of this Hamiltonian W' give us the vdW shifts and modifications of the widths, *but not the feeding of any state a by atoms leaving upper states n, as detailed in equation (38).*

7 Effective Hamiltonian for an atom near an interface

We have to come back at the beginning of the calculation. Let us call $H_0 = H_{\mathrm{at}} + H_{\mathrm{R}}$ the free Hamiltonian, without interaction between the atom and the reservoir (reservoir = vacuum + surface). The eigen states are: $|a,I\rangle$, their energy being: $E_a + E_I = \hbar(\omega_a + \omega_I)$. Capital letters denote eigenstates of the reservoir, small letters, eigenstates of the atom. The interaction potential between the atom and the field is: $V = -\boldsymbol{\mu}\cdot\mathbf{D}(\mathbf{r}_0)$ (Eq. (3)). We want to find an Hamiltonian H_{eff} for the atom in which is taken into account the effect of the reservoir and more precisely an effective atomic Hamiltonian describing the effect of the surface $H^{\mathrm{surf}}_{\mathrm{eff}}$. We want not only its diagonal elements (vdW shifts are already found (see Eqs. (29–31)) and the modification by the surface of transition rates (see Eqs. (33–35)), but also the *mean effect of the reservoir on off-diagonal* *elements.* W', as defined above, is purely diagonal and non-Hermitian (see Eqs. (44–46)).

One obtains an off-diagonal element for the atom's Hamiltonian by taking the mean value over the reservoir states of the corresponding off-diagonal element of the total Hamiltonian: $H = H_0 + V = H_{\rm at} + H_{\rm R} + V$:

$$\sum_I p(I)\left\langle a, I\left|H_0+V\right|b, I\right\rangle = \sum_I p(I)\left\langle a\left|H^I_{\rm eff}\right|b\right\rangle = \left\langle a\left|\sum_I p(I)H^I_{\rm eff}\right|b\right\rangle \quad (47)$$

(here $p(I) = {\rm e}^{-E_I/kT}/Z$, if we suppose the reservoir at thermal equilibrium at temperature T).

So we look for an Hamiltonian:

$$H_{\rm eff} = \sum_I p(I)H^I_{\rm eff}, \quad (48)$$

with the following properties:

(i) *hermitic*,
(ii) giving the same eigen-values that H, with the same degeneracy, *at least at second order in V.* (We have calculated the shift of any atomic level due to the surface taking the second order perturbation in V),
(iii) *which does not act between two different states I and J of the reservoir.* That comes from the definition of the trace (see Eq. (47)): $H^I_{\rm eff}$ acts only inside the I-multiplicity of the reservoir.

Such a calculation is classical in atom-field interactions (see [26], p. 41, and references therein). One has to find an unitary transformation $T = {\rm e}^{{\rm i}S}$, with an operator S chosen to be non-diagonal on the field states. Let us report the result obtained at second order in V:

$$\begin{aligned}\langle a|H^I_{\rm eff}|b\rangle &= (E_I + E_a\delta_{ab}) + \langle a, I|V|b, I\rangle \\ &\quad + \frac{1}{2}\sum_{n,N\neq I}\langle a, I|V|n, N\rangle\,\langle n, N|V|b, I\rangle \\ &\quad \times\left[\frac{1}{E_I+E_a-E_N-E_n}+\frac{1}{E_I+E_b-E_N-E_n}\right], \quad (49)\end{aligned}$$

where the energies of the two levels play a symmetric role.

The first term gives the energy of the free system, when $a = b$.

The second term is zero because the interaction potential: $V = -\boldsymbol{\mu}\cdot\mathbf{D}(\mathbf{r}_0) = -\mu_\alpha D_\alpha$ is made of products of non-diagonal operators (D_α in the basis of field-states as well as μ_α in the basis of atomic states).

When $E_a = E_b$, if $|a\rangle$ is a non-degenerate state, the third term will give the second order correction like it is obtained from perturbation theory. We can write it, after doing the statistic average over the reservoir states:

$$\langle a|H_{\rm eff}|a\rangle = {\rm P}\sum_{I,N,n} p(I)\langle a, I|V|n, N\rangle\langle n, N|V|a, I\rangle \times\left[\frac{1}{E_I+E_a-E_N-E_n}\right], \quad (50)$$

where P denotes the principal part.

This result has already been obtained (see Eqs. (12, 13)). For the contribution of the surface (anisotropic or isotropic), we can write (see Eqs. (24–31)):

$$\delta E^{\rm surf}_a = \left\langle a\left|H^{\rm surf}_{\rm eff}\right|a\right\rangle = \langle a\left|W(a)\right|a\rangle. \quad (51)$$

When $E_a \neq E_b$, we can now write the matrix elements of $H^{\rm surf}_{\rm eff}$. Formula (49) gives us:

$$\left\langle a\left|H^{\rm surf}_{\rm eff}\right|b\right\rangle = \left\langle a\left|\frac{1}{2}(W(a)+W(b))\right|b\right\rangle. \quad (52)$$

When $|a\rangle$ is a degenerate level, we obtain in the same way the matrix elements in the a-multiplicity:

$$\left\langle a\left|H^{\rm surf}_{\rm eff}\right|a'\right\rangle = \langle a\left|W(a)\right|a'\rangle. \quad (53)$$

8 Application: the case of cesium $6{\rm D}_{3/2}$ level and sapphire

The key-point is that transition $\omega_{na} = -12.147$ μm from $6{\rm D}_{3/2}$ to $7{\rm P}_{1/2}$ of cesium is resonant with one of the absorption frequencies of sapphire surface.

We want to evaluate the resonant part, which is the main contribution to the shift for this excited state [27]. Formulas (24–26) are written in function of the Cartesian components of dipole:

$$\begin{aligned}\delta E^{\rm res}_a(\theta) = -\frac{1}{16d^3}\sum_n A'_\theta(\omega_{na})\left|\mu^{an}_x\right|^2 + B'_\theta(\omega_{na})\left|\mu^{an}_y\right|^2 \\ + \left[A'_\theta(\omega_{na}) + B'_\theta(\omega_{na})\right]\left|\mu^{an}_z\right|^2 \quad (54)\end{aligned}$$

with

$$\begin{aligned}A'_\theta(\omega_{na}) &= \int_0^{2\pi}\frac{{\rm d}\varphi}{\pi}2\left[{\rm Re}R^{\rm st}_\theta(\varphi,\omega_{na})\right]\cos^2\varphi, \\ B'_\theta(\omega_{na}) &= \int_0^{2\pi}\frac{{\rm d}\varphi}{\pi}2\left[{\rm Re}R^{\rm st}_\theta(\varphi,\omega_{na})\right]\sin^2\varphi. \quad (55)\end{aligned}$$

The label a represents several quantum numbers of the free atom. For example, the level $6{\rm D}_{3/2}$ has $J = 3/2$, $L = 2$, $S = 1/2$, $n = 6$. We will consider first that the van der Waals interaction is a small perturbation to the free-atom Hamiltonian, this one including the fine structure term: so, eigen-vectors of the free atom are labelled $|\tau, J, M\rangle$. We consider first the cesium atom without hyperfine structure: indeed, the vdW surface interaction does not couple to the nuclear spin, and the hyperfine energy is small compared to the energy scale relevant to the sapphire resonance. One has to add the hyperfine correction once found the new eigen-states, after coupling with the surface.

So, levels a, a', ... will be here levels $|\tau, J, M\rangle$, with $J = 3/2$.

Among all the transitions in emission, we will keep only the ($6{\rm D}_{3/2} \rightarrow 7{\rm P}_{1/2}$) one, which has the larger transition dipole moment [18]: consequently, the only coupled levels n, n', ... taken into account here will be levels $|\tau', J', M'\rangle$, with $J' = 1/2$ (level $7{\rm P}_{1/2}$).

In order to find the new eigen-values of the Hamiltonian, and their degeneracies, we have to write in the a-multiplicity ($2J+1$ degenerate levels before interaction with the reservoir (vacuum+surface)) the contribution of the surface to the effective atomic Hamiltonian defined in Section 7.

The diagonal elements are given by equations (29–31). Keeping only the resonant part:

$$\delta E_a^{\rm res}(\theta) = \left\langle a \middle| H_{\rm eff}^{\rm surf,res} \middle| a \right\rangle = \langle a\,|W^{\rm res}(a)|\,a\rangle$$
$$= \langle a\,|W_a^{\rm res}(\theta)|\,a\rangle\,. \quad (56)$$

In the same way, off-diagonal elements of the effective atomic Hamiltonian defined in the precedent section are:

$$\left\langle a \middle| H_{\rm eff}^{\rm surf,res} \middle| a' \right\rangle = \langle a\,|W_a^{\rm res}(\theta)|\,a'\rangle\,. \quad (57)$$

The operator $W^{\rm res}(a)$ is named now $W_a^{\rm res}(\theta)$ because we are interested here by the dependence on θ, which is no longer a fixed parameter. Let us remember its form (see Eq. (31)):

$$W_a^{\rm res}(\theta) = -\frac{1}{16d^3}[A'\mu_x|n\rangle\langle n|\mu_x + B'\mu_y|n\rangle\langle n|\mu_y + (A'+B')\mu_z|n\rangle\langle n|\mu_z]$$

$$W_a^{\rm res}(\theta) = -\frac{1}{16d^3}\left[\frac{A'+B'}{2}(2\mu^0|n\rangle\langle n|\mu^0 - \mu^+|n\rangle\langle n|\mu^- - \mu^-|n\rangle\langle n|\mu^+) + \frac{A'-B'}{2}(\mu^+|n\rangle\langle n|\mu^+ + \mu^-|n\rangle\langle n|\mu^-)\right] \quad (58)$$

in which $A' = A'_\theta(\omega_{na})$, $B' = B'_\theta(\omega_{na})$, and $\mu^0 = \mu_z$, $\mu^\pm = \mp(\mu_x \pm {\rm i}\mu_y)/\sqrt{2}$.

We recall that, in the cesium-sapphire case, only one degenerate level n is strongly coupled to the degenerate level a, so we keep only that level in the sum over n of equation (54).

Calculating numerically the Fresnel coefficient for $\omega \approx \omega_{na}$ and a given value of θ, it is possible with equations (57, 58) to obtain all the matrix elements for the $6{\rm D}_{3/2}$ level of cesium (coupled to $7{\rm P}_{1/2}$) and to diagonalise the Hamiltonian in order to find the new eigenvalues and the new eigen-vectors. For $\theta \neq 0$, A' is different from B', and the Hamiltonian (58) couples levels $|\tau, J, M\rangle$ and $|\tau, J, M'\rangle$ such that $M - M' = \pm 2$, and the two degenerate levels are no longer the $|+M\rangle$ and $|-M\rangle$ sub-levels.

Degeneracy is not completely lifted by anisotropy, *as one could expect from the fact that this atomic state has an half-integer spin*: all levels remain two-fold degenerate, like in isotropic case. For a level with an integer-spin, degeneracy would be completely lifted when θ is different from zero (Kramers theorem, see [28]).

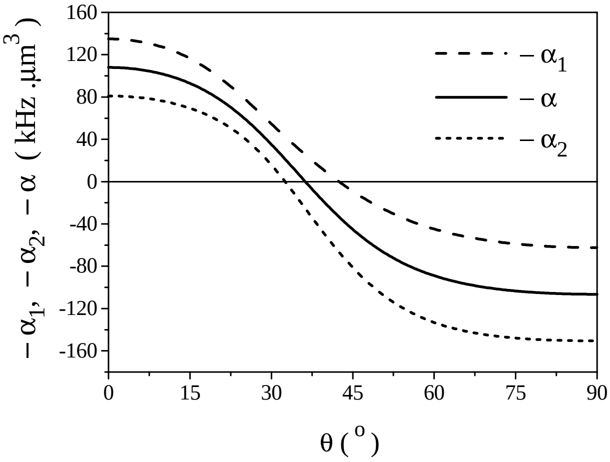

Fig. 4. Resonant part of the vdW shifts ($\delta E_i = -\alpha_i/d^3$) for the eigenstates $\mathbf{v}_1$ and $\mathbf{v}_2$ of cesium near a sapphire interface, and their half-sum in function of θ.

The expressions of the two degenerate eigen-values (contribution of the resonant part of the vdW shift) are:

$$\delta E_{1,2}^{\rm res}(\theta) = -\frac{1}{16d^3}|\langle \tau, J=3/2 \parallel \boldsymbol{\mu} \parallel \tau', J'=1/2\rangle|^2 \times \frac{A'+B'}{6}\left[1 \mp {\rm sgn}(A'+B')\frac{1}{4}\sqrt{1+3\Delta^2}\right] \quad (59)$$

in which $\Delta = (A'-B')/(A'+B')$ (subscript 1 is for the sign ($-$), subscript 2 for the sign ($+$)).

To report the variations of $\delta E_{1,2}^{\rm res}(\theta)$ and their half-sum in function of θ, we write: $\delta E_i^{\rm res} = \hbar\delta\omega = -\alpha_i/d^3$. For $\theta = 0$, previous calculations [27] give us the mean value $\alpha = (\alpha_1 + \alpha_2)/2$ in kHz μm^3 for the transition $6{\rm D}_{3/2}$ to $7{\rm P}_{1/2}$:

$$\alpha(\theta = 0) = -108\ {\rm kHz}\,\mu{\rm m}^3.$$

That gives the scale of our graph giving: $-\alpha(\theta)$, $-\alpha_1(\theta)$, $-\alpha_2(\theta)$, (or else the shifts in kHz, in function of θ, when the atom is located at a distance of one micrometer from the surface) (Fig. 4).

The mean value of the two twice-degenerate shifts has the sign of $-(A'+B')$. It is positive for the cylindrical symmetry ($\theta = 0$). We see in Figure 4 that, for the $6{\rm D}_{3/2}$ level, this sign is changing when $\theta = 36°25$. So, *the van der Waals potential, repulsive for an angle* $\theta < 36°25$*, becomes attractive for* $\theta > 36°25$.

When $\theta = 0$, the upper curve ($-\alpha_1$) gives the shift of the degenerate level $\mathbf{u}_1$ (*e.g.* $M = -1/2$) and ($-\alpha_2$) gives the shift of the degenerate level $\mathbf{u}_2$ ($M = +3/2$).

For other angles, we can write the rotation matrix giving the new degenerate eigenstates $\mathbf{v}_1$ and $\mathbf{v}_2$ in the basis $\mathbf{u}_1$, $\mathbf{u}_2$:

$$\begin{pmatrix} \cos\beta & -\sin\beta \\ \sin\beta & \cos\beta \end{pmatrix}$$

with:

$$\cos\beta = \frac{\Delta\sqrt{3}}{\sqrt{\eta^2 + 3\Delta^2}} \quad \text{and} \quad \sin\beta = \frac{\eta}{\sqrt{\eta^2 + 3\Delta^2}}\,\cdot$$

In these formulas: $\eta = \sqrt{1+3\Delta^2} - 1$, and Δ has been defined above in equation (59).

Of course, to calculate the static limit of Fresnel coefficient, we have used experimental data of sapphire: the uncertainties over the values of ordinary and extraordinary dielectric constants, as well as the position of absorption frequency of sapphire at 12.15 μm, are discussed in [27].

If an experiment could be done (using different cells whose sapphire windows would be cut at different angles with optic axis, which is not easy to realize), it would become possible to determine more accurately the frequency of the surface-resonance of sapphire: for an angle depending *only on this frequency*, the vdW potential becomes attractive, and that should appear in the selective reflection signal [19]. The experiment has been done in our group for only the two limit angles: $\theta = 0°$ ($C_\perp$) and $\theta = 90°$ ($C_\parallel$) [27–29].

To get the total eigen-values and corresponding eigenstates of cesium 6D$_{3/2}$ atom interacting with sapphire, one has to combine the vdW interaction with the hyperfine Hamiltonian. This gives a diagonalisation of the total Hamiltonian which will depend on the atom-surface distance d. At long distances, the eigen-states and eigenvalues are those of the hyperfine Hamiltonian: $|\tau, J = 3/2, F, M_F\rangle$. When the atom approaches the surface, the vdW interaction grows, and, after an intermediate complicated situation, takes it over at very short distances, where eigen-states and eigen-values become: $\mathbf{v}_1$, $\mathbf{v}_2$ and $\delta E^{\mathrm{res}}_{1,2}(\theta)$.

9 Conclusion

In this paper, we have presented the quantum-mechanical theory of van der Waals interactions between atoms in ground or excited state and birefringent dielectric surfaces. One has shown that, when there is a resonant coupling between excited atoms and dielectric surface resonances, an adequate choice of the direction of the C-axis allows one to shift the surface resonance and then, tune the atom-surface interactions, affording for an engineering of the surface forces. Also the symmetry of the atom wavefunction is broken by the surface near-field: while, for an isotropic dielectric, a cylindrical symmetry is kept, this is no longer true for a birefringent dielectric with an arbitrary orientation of the C-axis. This makes the dynamic study of an atom moving near a birefringent dielectric a quite difficult problem, similar to the one encountered in collisional studies, in which the atom quantization axis is rotating as a function of the distance to the surface.

Extensions of our work could include a detailed analysis of the retarded interactions with birefringent surfaces (either of the Casimir-Polder type, or of the resonant type). Another extension concerns the higher-order contributions in the atom-surface resonant coupling, which could turn *on* or *off* the atom-surface resonance, due to the huge vdW atomic shift at close distances. This might produce *non-monotonic* ($\neq 1/z^3$) *vdW shifts*: energy levels crossing or anticrossing, van der Waals wells with possible long-range atom trapping, etc.

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Appendix A: Calculation of “Fresnel coefficient” in the quasi-static limit

We report here the calculation of the electrostatic Fresnel coefficient (see geometry given in Figs. 1–3).

We are looking for solutions of Maxwell equations in the quasi-static limit:

$$\mathrm{div}\,\mathbf{D} = 0$$
$$\mathbf{rot}\,\mathbf{E} = 0 \Leftrightarrow \exists V \text{ such as } \mathbf{E} = -\mathbf{grad}V.$$

In the vacuum, $\mathbf{D} = \mathbf{E}$. Into the uniaxial dielectric, $\mathbf{D} = (\varepsilon)\mathbf{E}$ with:

$$(\varepsilon) = \begin{pmatrix} \varepsilon_0 & 0 & 0 \\ 0 & A & C \\ 0 & C & B \end{pmatrix} \cdot \qquad (A.1)$$

If θ is the angle between the normal to the surface and the principal optic axis (with $0 \le \theta \le \pi/2$), we have:

$$A = \varepsilon_0 \cos^2\theta + \varepsilon_e \sin^2\theta,\ \ B = \varepsilon_0 \sin^2\theta + \varepsilon_e \cos^2\theta,$$
$$C = (\varepsilon_0 - \varepsilon_e)\sin\theta\cos\theta. \qquad (A.2)$$

We look for solutions of the form “plane waves” with real wave-vector components in the interface in the quasi-static limit $\omega/c \to 0$. So, we try:

- above the interface ($0 < z < d$), an electrostatic potential:

  $$V_0(\mathbf{r}) = V_0^+ \mathrm{e}^{\mathrm{i}\mathbf{k}_0^+\cdot\mathbf{r}} + V_0^- \mathrm{e}^{\mathrm{i}\mathbf{k}_0^-\cdot\mathbf{r}} \qquad (A.3)$$

  (superscript ($-$) means “incident”, ($+$) means “reflected”),
- into the uniaxial dielectric ($z < 0$), an electrostatic potential:

  $$V_1(\mathbf{r}) = V_1^- \mathrm{e}^{\mathrm{i}\mathbf{k}_1^-\cdot\mathbf{r}}. \qquad (A.4)$$

Why an unique value of the wave-vector in an anisotropic media? We will show below that the “dispersion equation” in the birefringent media gives an unique value for the “wave-vector” in quasi-static limit (corresponding to the extraordinary wave of the retarded-case). We can see an example in Appendix B, where we have calculated the two wave-vectors in anisotropic media in the simplest case: $\theta = 0$.

All the “wave-vectors” must have the same components along the interface ($\mathbf{K}$: $K_x = K\cos\varphi, K_y = K\sin\varphi$), because the continuity of the potential in the interface ($z = 0$) must be satisfied for every point (x, y). The z-component is then defined by Maxwell equations in function of K for each media. We write:

$$\mathbf{k}_0^\pm = \mathbf{K} \pm W_0\hat{\mathbf{z}},$$
$$\mathbf{k}_1^- = \mathbf{K} - W_1\hat{\mathbf{z}}. \qquad (A.5)$$

In the vacuum, for $0 < z < d$: $\mathrm{div}\,\mathbf{E} = -\Delta V = 0 \Rightarrow K^2 + W_0^2 = 0$, and then: $W_0 = \mathrm{i}K$ ($K > 0$) ensures the "reflected" potential to vanish at infinity.

Into the birefringent media, for $z < 0$: $\mathrm{div}(\varepsilon)\mathbf{E} = 0$, with $\mathbf{E} = -\boldsymbol{\nabla} V$, gives a second degree equation:

$$B\frac{W_1^2}{K^2} - 2C\sin\varphi\frac{W_1}{K} + \cos^2\varphi + A\sin^2\varphi = 0$$

whose solutions are:

$$\frac{W_1}{K} = \frac{C}{B}\sin\varphi \pm \mathrm{i}\frac{\sqrt{-\Delta}}{B},$$

where

$$\begin{aligned}\Delta &= C^2\sin^2\varphi - B\left(\cos^2\varphi + A\sin^2\varphi\right)\\ &= -\varepsilon_0\varepsilon_e\left(1 + \frac{\varepsilon_0 - \varepsilon_e}{\varepsilon_e}\sin^2\theta\cos^2\varphi\right).\end{aligned} \tag{A.6}$$

Δ is *a priori* negative when the two dielectric constants are real of the same sign. In a dispersive media, they are complex functions of the frequency, but they take purely real positive values for imaginary frequencies, and we need to have the value of Fresnel coefficient only in this case (see integrals in Eqs. (13)).

We keep only the solution with $\mathrm{Im}W_1 > 0$. We can always choose the orientation of $\hat{\mathbf{x}}$ (the perpendicular to the optic axis which lies in the interface) in such a way that $(\varepsilon_0 - \varepsilon_e)\sin\varphi$ – and then $\mathrm{Re}W_1$ – will be positive. Finally, we can write:

$$B\frac{W_1}{K} - C\sin\varphi = +\mathrm{i}\sqrt{\varepsilon_0\varepsilon_e\left(1 + \delta\sin^2\theta\cos^2\varphi\right)}. \tag{A.7}$$

In equations (A.7), we have used: $(\varepsilon_0 - \varepsilon_e)/\varepsilon_e = \delta$.

Now, we write the boundary conditions at the interface for the tangential component of $\mathbf{E}$ (or equivalently for the potential) and for the normal component of $\mathbf{D}$

$$\begin{aligned}V_0^+ + V_0^- &= V_1^-,\\ \mathrm{i}W_0\left(V_0^+ - V_0^-\right) &= \left[C\left(\mathrm{i}K\sin\varphi\right) + B\left(-\mathrm{i}W_1\right)\right]V_1^-.\end{aligned}$$

For a given "incident" field, defining $r = V_0^+/V_0^-$ and $t = V_1^-/V_0^-$, this gives the system:

$$\begin{aligned}r + 1 &= t,\\ r - 1 &= -\mathrm{i}\left[C\sin\varphi - \frac{W_1}{K}\right]t\\ &= -t\sqrt{\varepsilon_0\varepsilon_e\left(1 + \delta\sin^2\theta\cos^2\varphi\right)},\end{aligned} \tag{A.8}$$

where we have used equation (A.7) and we obtain:

$$\begin{aligned}r &= \frac{1 - \sqrt{\varepsilon_0\varepsilon_e\left(1 + \delta\sin^2\theta\cos^2\varphi\right)}}{1 + \sqrt{\varepsilon_0\varepsilon_e\left(1 + \delta\sin^2\theta\cos^2\varphi\right)}},\\ t &= \frac{2}{1 + \sqrt{\varepsilon_0\varepsilon_e\left(1 + \delta\sin^2\theta\cos^2\varphi\right)}}\cdot\end{aligned} \tag{A.9}$$

We are looking for the reflection coefficient for the electric field, not for the potential. With $\mathbf{E}_0^+(\mathbf{r}) = -\mathrm{i}\mathbf{k}_0^+ V_0^+(\mathbf{r})$ and $\mathbf{E}_0^-(\mathbf{r}) = -\mathrm{i}\mathbf{k}_0^- V_0^-(\mathbf{r})$, the electric fields are longitudinal (along $\mathbf{k}_0^\pm$). They have two components: $E_{0K}^\pm$ and $E_{0z}^\pm$, respectively parallel to $\mathbf{K}$ and perpendicular to the surface. How to define an electrostatic reflection coefficient and how to be sure that this coefficient is the quasi-static limit of a Fresnel coefficient defined for plane waves?

Only p-polarised electric fields have a z-component, like electrostatic fields. If we make the z-components of the unit vectors $\hat{\mathbf{p}}_0^\pm$ equal ($\hat{\mathbf{p}}_0^\pm = k_0^{-1}(\mp W_0\hat{\mathbf{K}} + K\hat{\mathbf{z}})$), we have, in the retarded case:

$$\frac{E_z^{\mathrm{R}}}{E_z^{\mathrm{I}}} = \frac{E_z^{p_0^+}}{E_z^{p_0^-}} = \frac{E^{p_0^+}}{E^{p_0^-}}\cdot$$

Then, the ratio of z-components of "reflected" and "incident" fields in the non-retarded case must be the limit for $\omega/c \to 0$ of the same ratio in retarded case:

$$\begin{aligned}\lim\frac{E_z^{\mathrm{R}}}{E_z^{\mathrm{I}}} = \frac{E_{0z}^+}{E_{0z}^-} &= \frac{-\mathrm{i}W_0V_0^+}{+\mathrm{i}W_0V_0^-} = -r\\ &= \frac{\sqrt{\varepsilon_0\varepsilon_e\left(1 + \delta\sin^2\theta\cos^2\varphi\right)} - 1}{\sqrt{\varepsilon_0\varepsilon_e\left(1 + \delta\sin^2\theta\cos^2\varphi\right)} + 1} = -\frac{E_{0K}^+}{E_{0K}^-},\end{aligned}$$

where r has been defined in equation (A.9).

On the other hand, s-polarised electric fields cannot have a static limit different of zero. The choice we made to calculate electrostatic modes: $\mathbf{E}_0^+(\mathbf{r}) = -\mathrm{i}\mathbf{k}_0^+ V_0^+(\mathbf{r})$ and $\mathbf{E}_0^-(\mathbf{r}) = -\mathrm{i}\mathbf{k}_0^- V_0^-(\mathbf{r})$ implies that $\mathbf{E}_0$ belongs to the plane $(\mathbf{K}, \hat{\mathbf{z}})$ and cannot be parallel to $\hat{\mathbf{s}} = \hat{\mathbf{K}} \times \hat{\mathbf{z}}$. More exactly, this is only possible for vanishing components of $\mathbf{k}_0^\pm$ ($W_0 = \mathrm{i}K = 0$), and then zero fields. So, we will consider in equations (15) that we have only p-waves when looking for the static limit. We obtain then from equations (15):

$$\lim R^{pp} = \lim\frac{E_p^{\mathrm{R}}}{E_p^{\mathrm{I}}} = \lim\frac{E_z^{\mathrm{R}}}{E_z^{\mathrm{I}}} = \frac{E_{0z}^+}{E_{0z}^-}\cdot$$

We will call this limit $R_\theta^{\mathrm{st}}(\varphi)$ (see Eq. (17)).

From equations (15), we have also: $\lim R^{\mathrm{sp}} = 0$.

Appendix B: Calculation of the retarded Fresnel coefficients in the simple case of the optic axis perpendicular to the surface. Limit of these coefficients in non-retarded case

In the bulk of an anisotropic media, Maxwell equations written for a plane wave of wave-vector $\mathbf{k}$ lead to the dispersion equation:

$$k_0^2\mathbf{D} - k^2\mathbf{E} + (\mathbf{k}\cdot\mathbf{E})\mathbf{k} = \mathbf{0} \tag{B.1}$$

with: $k_0^2 = \omega^2/c^2$ and $\mathbf{D} = (\varepsilon)\mathbf{E}$, where (ε) is given in Appendix A (Eq. (A.1)). In the two cases $\theta = 0$, $\theta = \pi/2$, the tensor is diagonal and we write it under the form:

$$(\varepsilon) = \begin{pmatrix} \varepsilon_0 & 0 & 0 \\ 0 & A & 0 \\ 0 & 0 & B \end{pmatrix},$$

with A, B, defined in Appendix A (Eq. (A.2)).

The components of $\mathbf{k}$ in the basis $(\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}})$ are respectively: $(u = K\cos\varphi, v = K\sin\varphi, k_z)$. The x, y-components are determined by continuity with the same components of the wave-vector in vacuum: $\mathbf{k}_0$. Our problem here is to find which values can take k_z for a given $\mathbf{K}(u, v)$.

Projecting equation (B.1), one obtains:

$$\begin{aligned} &k_0^2\varepsilon_0 E_x - k^2 E_x + (uE_x + vE_y + k_z E_z)u = 0, \\ &k_0^2 A E_y - k^2 E_y + (uE_x + vE_y + k_z E_z)v = 0, \\ &k_0^2 B E_z - k^2 E_z + (uE_x + vE_y + k_z E_z)k_z = 0. \end{aligned} \qquad \text{(B.2)}$$

Looking for a non-zero solution for the field, we have to write the condition:

$$\det \begin{pmatrix} k_0^2\varepsilon_0 - v^2 - k_z^2 & uv & uk_z \\ uv & k_0^2 A - u^2 - k_z^2 & vk_z \\ uk_z & vk_z & k_0^2 B - K^2 \end{pmatrix} = 0.$$

This leads to a peculiar quartic equation, taking the form: $k_z^4 - \Sigma k_z^2 + \Pi = 0$.

When $\theta = 0$ ($A = \varepsilon_0$, $B = \varepsilon_e$), the values of Σ and Π are respectively:

$$\begin{aligned} \Sigma &= 2k_0^2\varepsilon_0 - K^2\frac{\varepsilon_0}{\varepsilon_e} - K^2, \\ \Pi &= \left(k_0^2\varepsilon_0 - K^2\right)\left(k_0^2\varepsilon_0 - K^2\frac{\varepsilon_0}{\varepsilon_e}\right)\cdot \end{aligned}$$

Two solutions appear, which are independent of φ:

$$\begin{aligned} \text{the ordinary wave: } k_z^2 &= W_1^2 = k_0^2\varepsilon_0 - K^2, \\ \text{the extraordinary wave: } k_z^2 &= W_1'^2 = k_0^2\varepsilon_0 - K^2\frac{\varepsilon_0}{\varepsilon_e}\cdot \end{aligned} \qquad \text{(B.3)}$$

For $\theta = \pi/2$ ($A = \varepsilon_e, B = \varepsilon_0$), one obtains in the same way:

$$\begin{aligned} W_1^2 &= k_0^2\varepsilon_0 - K^2, \\ W_1'^2 &= k_0^2\varepsilon_e - K^2 + \left(1 - \frac{\varepsilon_e}{\varepsilon_0}\right)K^2\sin^2\varphi. \end{aligned} \qquad \text{(B.4)}$$

Now, we have to write boundary conditions at the interface to obtain reflection coefficients. In the vacuum ($z > 0$) we write the field like the sum of an incident (s or p) field and a reflected (s and p) one. In the media, we write the field like a sum of an ordinary field and an extraordinary one. For this purpose, we have to specify the polarisations of these last fields which are no more TE or TM, unlike in the vacuum. We show here how to do only for the case of the optical axis perpendicular to the interface. (There is no more difficulty to calculate the solution when the axis C lies in the interface, but it is much longer).

We write that the displacement fields of the ordinary and extraordinary waves are transverse: $\mathbf{k}_1 \cdot \mathbf{D}_1 = 0$ and $\mathbf{k}_1' \cdot \mathbf{D}_1' = 0$, and we write their respective polarisations: $\mathbf{D}_1$ is perpendicular to $\hat{\mathbf{C}}$ (and to $\mathbf{k}_1$); $\mathbf{D}_1'$ is in the contrary situated in the plane $(\hat{\mathbf{C}}, \mathbf{k}_1')$, then perpendicular to the vector $\hat{\mathbf{C}} \wedge \mathbf{k}_1'$ (and perpendicular to $\mathbf{k}_1'$).

When $\theta = 0$, the optical axis is parallel to Oz. For the ordinary wave, with the components of $\mathbf{D}_1$ $(D_{1x} = \varepsilon_0 E_{1x}, D_{1y} = \varepsilon_0 E_{1y}, D_{1z} = \varepsilon_e E_{1z})$ and those of $\mathbf{k}_1(u, v, -W_1)$, we can write:

$$\begin{aligned} D_{1z} &= 0, \\ u\left(\varepsilon_0 E_{1x}\right) + v\left(\varepsilon_0 E_{1y}\right) &= 0. \end{aligned}$$

This gives the polarisation of the electromagnetic ordinary field:

$$\mathbf{E}_1 = \left|\begin{array}{l} E_{1x} \\ E_{1y} = -\dfrac{u}{v}E_{1x} \\ E_{1z} = 0 \end{array}\right. \cdot \qquad \text{(B.5)}$$

For the extraordinary wave, with the components of $\mathbf{D}_1'$ $\left(D_{1x}' = \varepsilon_0 E_{1x}', D_{1y}' = \varepsilon_0 E_{1y}', D_{1z}' = \varepsilon_e E_{1z}'\right)$ and those of $\mathbf{k}_1'(u, v, -W_1')$, we have:

$$\begin{aligned} \mathbf{k}_1' \cdot \mathbf{D}_1' = 0 &\Rightarrow u\varepsilon_0 E_{1x}' + v\varepsilon_0 E_{1y}' - W_1'\varepsilon_e E_{1z}' = 0 \\ \left(\hat{\mathbf{C}} \wedge \mathbf{k}_1'\right) \cdot \mathbf{D}_1' &= \left(\hat{\mathbf{z}} \wedge \mathbf{k}_1'\right) \cdot \mathbf{D}_1' \\ &= -v\varepsilon_0 E_{1x}' + u\varepsilon_0 E_{1y}' = 0 \end{aligned}$$

which gives the polarisation of the extraordinary electromagnetic field:

$$\mathbf{E}_1' = \left|\begin{array}{l} E_{1x}' \\ E_{1y}' = \dfrac{v}{u}E_{1x}' \\ E_{1z}' = \dfrac{\varepsilon_e}{\varepsilon_0}\dfrac{K^2}{uW_1'}E_{1x}' \end{array}\right. \cdot \qquad \text{(B.6)}$$

The respective magnetic fields can be deduced immediately:

$$\mathbf{B}_1 = \left|\begin{array}{l} B_{1x} = -\dfrac{W_1}{k_0}\dfrac{u}{v}\dfrac{E_{1x}}{c} \\ B_{1y} = -\dfrac{W_1}{k_0}\dfrac{E_{1x}}{c} \\ B_{1z} = -\dfrac{K^2}{vk_0}\dfrac{E_{1x}}{c} \end{array}\right., \quad \mathbf{B}_1' = \left|\begin{array}{l} B_{1x}' = \dfrac{v}{u}\dfrac{k_0}{W_1'}\varepsilon_0\dfrac{E_{1x}'}{c} \\ B_{1y}' = -\dfrac{k_0}{W_1'}\varepsilon_0\dfrac{E_{1x}'}{c} \\ B_{1z}' = 0 \end{array}\right. \cdot \qquad \text{(B.7)}$$

We first suppose an incident wave in the vacuum with one s (or p)-polarisation: $E_{0s}^-\hat{\mathbf{s}}$ (or $E_{0p}^-\hat{\mathbf{p}}_0^-$) and its magnetic field: $B_{0p}^-\hat{\mathbf{p}}_0^-$ (or $B_{0s}^-\hat{\mathbf{s}}$). Reflected wave on the anisotropic surface will be a superposition of s and p-polarised waves: $E_{0s}^+\hat{\mathbf{s}} + E_{0p}^+\hat{\mathbf{p}}_0^+$, with their respective magnetic fields: $B_{0p}^+\hat{\mathbf{p}}_0^+ + B_{0s}^+\hat{\mathbf{s}}$.

One has: $\hat{\mathbf{k}}_0^{\pm} \wedge \hat{\mathbf{p}}_0^{\pm} = \hat{\mathbf{s}}$ and $\hat{\mathbf{k}}_0^{\pm} \wedge \hat{\mathbf{s}} = -\hat{\mathbf{p}}_0^{\pm}$. So:

$$B_{0p}^- = -\frac{E_{0s}^-}{c}, \quad B_{0p}^+ = -\frac{E_{0s}^+}{c}, \quad B_{0s}^+ = \frac{E_{0p}^+}{c}, \quad B_{0s}^- = \frac{E_{0p}^-}{c} \tag{B.8}$$

and also:

$$\hat{\mathbf{K}} \left| \begin{array}{l} \cos\varphi \\ \sin\varphi \\ 0 \end{array} \right. \quad \hat{\mathbf{s}} \left| \begin{array}{l} \sin\varphi \\ -\cos\varphi \\ 0 \end{array} \right. \quad \hat{\mathbf{p}}_0^- \left| \begin{array}{l} \dfrac{W_0}{k_0}\cos\varphi \\ \dfrac{W_0}{k_0}\sin\varphi \\ \dfrac{K}{k_0} \end{array} \right. \quad \hat{\mathbf{p}}_0^+ \left| \begin{array}{l} \dfrac{-W_0}{k_0}\cos\varphi \\ \dfrac{-W_0}{k_0}\sin\varphi \\ \dfrac{K}{k_0} \end{array} \right. \cdot \tag{B.9}$$

We can write now the boundary conditions for each component of the electromagnetic field. One introduces the quantities: in the case of an *s*-incident electric field,

$$R^{ss} = \frac{E_{0s}^+}{E_{0s}^-}, \quad R^{ps} = \frac{E_{0p}^+}{E_{0s}^-}, \quad \alpha = \frac{E_{1x}}{E_{0s}^-}, \quad \beta = \frac{E'_{1x}}{E_{0s}^-} \tag{B.10}$$

in the case of a *p*-incident field,

$$R^{pp} = \frac{E_{0p}^+}{E_{0p}^-}, \quad R^{sp} = \frac{E_{0s}^+}{E_{0p}^-}, \quad \gamma = \frac{E_{1x}}{E_{0p}^-}, \quad \delta = \frac{E'_{1x}}{E_{0p}^-} \cdot \tag{B.11}$$

In each case, we obtain a system of six equations with four unknowns, the solution of which gives us the Fresnel coefficients.

S-system

Using equation (B.9), one gets:

$$\begin{aligned}
E_{1x} + E'_{1x} &= E_{0s}^-(\sin\varphi) + E_{0s}^+(\sin\varphi) \\
&\quad + E_{0p}^+\left(-\frac{W_0}{k_0}\cos\varphi\right) \\
E_{1y} + E'_{1y} &= E_{0s}^-(-\cos\varphi) + E_{0s}^+(-\cos\varphi) \\
&\quad + E_{0p}^+\left(-\frac{W_0}{k_0}\sin\varphi\right) \\
\varepsilon_e(E_{1z} + E'_{1z}) &= E_{0p}^+\left(\frac{K}{k_0}\right) \\
B_{1x} + B'_{1x} &= B_{0p}^-\left(\frac{W_0}{k_0}\cos\varphi\right) \\
&\quad + B_{0p}^+\left(-\frac{W_0}{k_0}\cos\varphi\right) + B_{0s}^+(\sin\varphi) \\
B_{1y} + B'_{1y} &= B_{0p}^-\left(\frac{W_0}{k_0}\sin\varphi\right) \\
&\quad + B_{0p}^+\left(-\frac{W_0}{k_0}\sin\varphi\right) + B_{0s}^+(-\cos\varphi) \\
B_{1z} + B'_{1z} &= B_{0p}^-\left(\frac{K}{k_0}\right) + B_{0p}^+\left(\frac{K}{k_0}\right) \cdot
\end{aligned} \tag{B.12}$$

This system can also be written, using equations (B.8, B.10):

$$\begin{aligned}
&\alpha + \beta = (1 + R^{ss})\sin\varphi - R^{ps}\frac{W_0}{k_0}\cos\varphi \\
&-\frac{\cos\varphi}{\sin\varphi}\alpha + \frac{\sin\varphi}{\cos\varphi}\beta = (1 + R^{ss})(-\cos\varphi) - R^{ps}\frac{W_0}{k_0}\sin\varphi \\
&\varepsilon_0\frac{K}{(\cos\varphi)W'_1}\beta = R^{ps}\frac{K}{k_0} \Rightarrow R^{ps} = \varepsilon_0\frac{k_0}{(\cos\varphi)W'_1}\beta \\
&\alpha\left(-\frac{W_1}{k_0}\frac{\cos\varphi}{\sin\varphi}\right) + \beta\left(\varepsilon_0\frac{k_0}{W'_1}\frac{\sin\varphi}{\cos\varphi}\right) = \\
&\qquad\qquad (R^{ss} - 1)\frac{W_0}{k_0}\cos\varphi + R^{ps}\sin\varphi \\
&\alpha\left(-\frac{W_1}{k_0}\right) + \beta\left(-\varepsilon_0\frac{k_0}{W'_1}\right) = \\
&\qquad\qquad (R^{ss} - 1)\frac{W_0}{k_0}\sin\varphi - R^{ps}\cos\varphi \\
&\alpha\frac{K}{k_0\sin\varphi} = (1 + R^{ss})\frac{K}{k_0} \Rightarrow (1 + R^{ss}) = \frac{\alpha}{\sin\varphi} \cdot
\end{aligned} \tag{B.13}$$

The third and sixth equations, when inserted in the first one, give the expected result $R^{ps} = 0$ (one cannot have: $W'_1 = -\varepsilon_0 W_0$) and then $\beta = 0$. The first and the fifth equations give now:

$$R^{ss} = \frac{W_0 - W_1}{W_0 + W_1} \tag{B.14}$$

whose static limit is zero, because then: $W_0, W_1 \rightarrow \mathrm{i}K$ (see Eqs. (A.5, B.3) when $k_0 \rightarrow 0$).

P-system

When the incident wave is a *p*-wave, the "continuity" of the six components at the boundary gives:

$$\begin{aligned}
E_{1x} + E'_{1x} &= E_{0p}^-\left(\frac{W_0}{k_0}\cos\varphi\right) + E_{0s}^+(\sin\varphi) \\
&\quad + E_{0p}^+\left(-\frac{W_0}{k_0}\cos\varphi\right) \\
E_{1y} + E'_{1y} &= E_{0p}^-\left(\frac{W_0}{k_0}\sin\varphi\right) \\
&\quad + E_{0s}^+(-\cos\varphi) + E_{0p}^+\left(-\frac{W_0}{k_0}\sin\varphi\right) \\
\varepsilon_e(E_{1z} + E'_{1z}) &= E_{0p}^-\left(\frac{K}{k_0}\right) + E_{0p}^+\left(\frac{K}{k_0}\right) \\
B_{1x} + B'_{1x} &= B_{0s}^-(\sin\varphi) + B_{0p}^+\left(-\frac{W_0}{k_0}\cos\varphi\right) \\
&\quad + B_{0s}^+(\sin\varphi) \\
B_{1y} + B'_{1y} &= B_{0s}^-(-\cos\varphi) + B_{0p}^+\left(-\frac{W_0}{k_0}\sin\varphi\right) \\
&\quad + B_{0s}^+(-\cos\varphi) \\
B_{1z} + B'_{1z} &= B_{0p}^+\left(\frac{K}{k_0}\right) \cdot
\end{aligned} \tag{B.15}$$

Using equations (B.8, B.11), these equations (B.15) can be written:

$$\gamma+\delta=(1-R^{pp})\left(\frac{W_0}{k_0}\cos\varphi\right)+R^{sp}\sin\varphi$$

$$\left(-\frac{\cos\varphi}{\sin\varphi}\right)\gamma+\left(\frac{\sin\varphi}{\cos\varphi}\right)\delta=$$
$$(1-R^{pp})\left(\frac{W_0}{k_0}\sin\varphi\right)-R^{sp}\cos\varphi$$

$$\varepsilon_0\left(\frac{k_0}{W_1'\cos\varphi}\right)\delta=1+R^{pp}$$

$$\gamma\left(-\frac{W_1}{k_0}\frac{\cos\varphi}{\sin\varphi}\right)+\delta\left(\varepsilon_0\frac{k_0}{W_1'}\frac{\sin\varphi}{\cos\varphi}\right)=$$
$$(1+R^{pp})\sin\varphi+R^{sp}\left(\frac{W_0}{k_0}\cos\varphi\right)$$

$$\gamma\left(-\frac{W_1}{k_0}\right)+\delta\left(-\varepsilon_0\frac{k_0}{W_1'}\right)=$$
$$-(1+R^{pp})\cos\varphi+R^{sp}\left(\frac{W_0}{k_0}\sin\varphi\right)$$

$$\gamma\left(\frac{1}{\sin\phi}\right)=R^{sp}. \tag{B.16}$$

The first and last equations, when combined with the third one, yield:

$$R^{pp}=\frac{\varepsilon_0W_0-W_1'}{\varepsilon_0W_0+W_1'}\cdot \tag{B.17}$$

The fourth one for example gives $R^{sp}=0$ (because one cannot have: $-W_1=W_0$).

Looking now for the electrostatic limit (see formulas (B.3)):

$$W_0\to\mathrm{i}K\quad W_1\to\mathrm{i}K\quad W_1'\to\mathrm{i}K\sqrt{\frac{\varepsilon_0}{\varepsilon_e}}$$

$$\lim R^{pp}=\frac{\sqrt{\varepsilon_0\varepsilon_e}-1}{\sqrt{\varepsilon_0\varepsilon_e}+1}=\frac{\bar{\varepsilon}-1}{\bar{\varepsilon}+1}=R^{\text{stat}}_{\theta=0}$$

We recover the image coefficient of reference [18] and also check that our electrostatic coefficient is the static limit of the Fresnel coefficient R^{pp}.

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