Dynamical Casimir–Polder interaction between a chiral molecule and a surface

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We develop a dynamical approach to study the Casimir–Polder force between a initially bare molecule and a magnetodielectric body at finite temperature. Switching on the interaction between the molecule and the field at a particular time, we study the resulting temporal evolution of the Casimir–Polder interaction. The dynamical self-dressing of the molecule and its population-induced dynamics are accounted for and discussed. In particular, we find that the Casimir–Polder force between a chiral molecule and a perfect mirror oscillates in time with a frequency related to the molecular transition frequency, and converges to the static result for large times.

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I. INTRODUCTION

Casimir and Casimir–Polder forces (CP) are electromagnetic interactions between neutral macroscopic bodies and/or molecules due to the quantum fluctuations of the electromagnetic field [1–3]. The presence of perfect boundaries (perfect conductors) modifies the possible wavelength of vacuum fluctuations and leads to observable effects like the lifetime and frequency shift of an atom in an excited state [4], the interatomic potential between two atoms [5], the anomalous gyromagnetic ratio [6, 7], which are all different from the vacuum case. The interaction between a ground-state molecule and a perfect electric mirror is always attractive while the interaction between an excited molecule and an perfect electric mirror shows an oscillating distance-dependence. This has been confirmed in measurements of the force between an excited ion and a metallic mirror [8, 9].

Recently, the attention in the literature has been directed towards chiral molecules which posses distinctive optical properties including optical rotation as well as circular dichroism. Chiral molecules are molecules without point or plane symmetry; the two distinct mirror images of a chiral molecule are called enantiomers. Many of the processes crucial to life involve chiral molecules whose chiral identity plays a central role in their chemical reactions, the wrong enantiomer reacts in a different way and does not produce the required result. Spectroscopically, enantiomers have identical properties and distinguishing between them is a non-trivial task when using normal spectroscopy. A frequently used method to separate enantiomers in an industrial setting is chiral chromotography [10]. Recently, several laser schemes have been proposed to separate mixtures of enantiomers, and the effect of molecular rotation on enantioseparation has been studied [11]. Furthermore Casimir–Polder forces between chiral molecules in absorptive and dispersive chiral medium have shown discriminatory effects, which might be used to separate enantiomers [12–17].

In this article, we consider the dynamical Casimir– Polder interaction between a chiral molecule and a metal or dielectric body at finite temperature using a dynamical approach, with the molecule exhibiting electric, magnetic and chiral polarizabilities. The dynamical CP force between an enantiomer and a perfect chiral mirror is a possible system for distinguishing and separating enantiomers, because the dispersion energy between these systems depends on the relative handedness of the molecule with respect to that of the molecules constituting the chiral mirror. Therefore, enantiomers that pass at low speeds near the chiral mirror will be attracted or repelled in opposite directions and will be separated based on their chirality.

We assume to switch on the interaction between the molecule and the field at a particular time and study the resulting time evolution of the Casimir–Polder interaction. Even if the interaction with the free field is always present, our assumption to switch on suddenly the interaction with the body-assisted field at $t_0 = 0$ can be a good approximation of the more realistic cases of a rapid change of some parameter characterizing the strength of the atom-field interaction or of putting the atom at some

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distance from the macroscopic body, obtaining a partially dressed atom or molecule [18]. The dynamics of the force could be observed in principle on time-scales of femto-seconds for typical molecules and nano-seconds for Rydberg atoms.

The dynamical self-dressing has been considered for an electric ground-state atom near an electric perfect conductor [19], or for a partially dressed atomic state [20]. Also, the dynamical CP interaction between a neutral atom and a real surface has been recently investigated [21]. The CP force of a chiral molecule near a body has so far been considered only in the static case [15]. In this paper, we consider the dynamical self-dressing for a chiral molecule near a body; our approach includes finite temperature, arbitrary geometries of the body and arbitrary internal molecular states. As a simple application, we consider the CP interaction between an initially bare ground-state chiral molecule and a perfect chiral plate at zero temperature. We will show that the Casimir-Polder interaction at large times can be attractive or repulsive depending on the chiralities of the molecule and the medium. This differs from the stationary CP interaction between an electric molecule and an electric perfect plate, which is always attractive [2, 22]. Furthermore, the time-dependent approach allows us to follow the temporal evolution of the CP force due to the initial conditions.

The article is organised as follows. In Sect. II, we consider the Heisenberg dynamics of the molecule and the body-assisted field, mutually coupled. Then, in Sect. III, we consider the dynamical Casimir–Polder interaction between a molecule with electric, magnetic and chiral responses and a body of arbitrary shape at finite temperature. In Sect. IV, we apply these results to a particular case: the dynamical CP interaction between an initially bare chiral ground-state molecule and a perfectly reflecting chiral plate at zero temperature. We close with some conclusion in Sect. V.

II. DYNAMICS OF THE MOLECULE AND THE BODY-ASSISTED FIELD

We consider the mutually coupled temporal evolution of a single molecule and the body-assisted field. The body-field system is prepared at uniform temperature T, and the molecule in an arbitrary incoherent superposition of internal energy eigenstates. The dynamics of the molecule can be described with time-dependent flip operators, defined by $A_{mn} = |m\rangle \langle n|$, where $|n\rangle$ is an energy eigenstate.

In order to evaluate the dynamical CP force between the molecule and the body, we must first solve the molecule-field dynamics to obtain the flip operators and the field operators in the Heisenberg picture. The total Hamiltonian is the sum of three terms, the molecule and the field Hamiltonians and the interaction term in the dipole approximation: $H = H_A + H_F + H_{AF}$, where

$$H_{A} = \sum_{n} E_{n} A_{nn}$$

$$H_{F} = \sum_{\lambda=e,m} \int d^{3}r \int_{0}^{\infty} d\omega \hbar \omega \mathbf{f}_{\lambda}^{\dagger}(\mathbf{r},\omega) \cdot \mathbf{f}_{\lambda}(\mathbf{r},\omega)$$

$$H_{AF} = -\mathbf{d} \cdot \mathbf{E}(\mathbf{r}_{A}) - \mathbf{m} \cdot \mathbf{B}(\mathbf{r}_{A})$$
(1)

where $\mathbf{f}_{\lambda}(\mathbf{r}, \omega)$ is the annihilation operator for the elementary electric and magnetic excitations of the system [15], **d** and **m** are respectively the molecule's electric and magnetic dipole moments, and \mathbf{r}_{A} the position of the molecule.

We introduce the Fourier component of the electric field $\mathbf{E}(\mathbf{r}, \omega)$, $\mathbf{E}(\mathbf{r}) = \int_0^\infty d\omega \mathbf{E}(\mathbf{r}, \omega) + h.c.$ The commutators between electromagnetic fields read

The commutators between electromagnetic fields read [15]:

$$\begin{bmatrix} \mathbf{E} (\mathbf{r}, \omega), \mathbf{E}^{\dagger} (\mathbf{r}', \omega') \end{bmatrix} = \frac{\hbar\mu_{0}}{\pi} \operatorname{Im} \mathbf{G} (\mathbf{r}, \mathbf{r}', \omega) \omega^{2} \delta (\omega - \omega')$$
$$\begin{bmatrix} \mathbf{E} (\mathbf{r}, \omega), \mathbf{B}^{\dagger} (\mathbf{r}', \omega') \end{bmatrix} = -\frac{i\hbar\mu_{0}}{\pi} \operatorname{Im} \mathbf{G} (\mathbf{r}, \mathbf{r}', \omega) \times \overleftarrow{\nabla}' \omega \delta (\omega - \omega')$$
$$\begin{bmatrix} \mathbf{B} (\mathbf{r}, \omega), \mathbf{E}^{\dagger} (\mathbf{r}', \omega') \end{bmatrix} = -\frac{i\hbar\mu_{0}}{\pi} \nabla \times \operatorname{Im} \mathbf{G} (\mathbf{r}, \mathbf{r}', \omega) \omega \delta (\omega - \omega')$$
$$\begin{bmatrix} \mathbf{B} (\mathbf{r}, \omega), \mathbf{B}^{\dagger} (\mathbf{r}', \omega') \end{bmatrix} = -\frac{\hbar\mu_{0}}{\pi} \nabla \times \operatorname{Im} \mathbf{G} (\mathbf{r}, \mathbf{r}', \omega) \times \overleftarrow{\nabla}' \delta (\omega - \omega')$$
$$\begin{bmatrix} \mathbf{B} (\mathbf{r}, \omega), \mathbf{B}^{\dagger} (\mathbf{r}', \omega') \end{bmatrix} = -\frac{\hbar\mu_{0}}{\pi} \nabla \times \operatorname{Im} \mathbf{G} (\mathbf{r}, \mathbf{r}', \omega) \times \overleftarrow{\nabla}' \delta (\omega - \omega')$$
(2)

where **G** is the classical Green tensor of the electromagnetic field and $\left[\mathbf{G} \times \overleftarrow{\nabla}'\right]_{ij} = \mathbf{G}_{ik}\varepsilon_{jkl}\overleftarrow{\partial}/\partial x'_l$, the Heisenberg equations for the coupled molecule–field dynamics read:

$$\dot{A}_{mn} = i\omega_{mn}A_{mn} + \frac{i}{\hbar}\mathbf{K}_{mn}\cdot\mathbf{E}\left(\mathbf{r}_{A}\right) + \frac{i}{\hbar}\mathbf{Q}_{mn}\cdot\mathbf{B}\left(\mathbf{r}_{A}\right)$$
$$\dot{\mathbf{E}}\left(\mathbf{r},\omega\right) = -i\omega\mathbf{E}\left(\mathbf{r},\omega\right) + \frac{i\mu_{0}}{\pi}\omega^{2}\mathrm{Im}\mathbf{G}\left(\mathbf{r},\mathbf{r}_{A},\omega\right)\cdot\mathbf{d}$$
$$+ \frac{\mu_{0}}{\pi}\omega\mathrm{Im}\mathbf{G}\left(\mathbf{r},\mathbf{r}_{A},\omega\right)\times\overleftarrow{\nabla}'\cdot\mathbf{m}$$
$$\dot{\mathbf{B}}\left(\mathbf{r},\omega\right) = -i\omega\mathbf{B}\left(\mathbf{r},\omega\right) + \frac{\mu_{0}}{\pi}\omega\nabla\times\mathrm{Im}\mathbf{G}\left(\mathbf{r},\mathbf{r}_{A},\omega\right)\cdot\mathbf{d}$$
$$- \frac{i\mu_{0}}{\pi}\nabla\times\mathrm{Im}\mathbf{G}\left(\mathbf{r},\mathbf{r}_{A},\omega\right)\times\overleftarrow{\nabla}'\cdot\mathbf{m}$$
(3)

where $\mathbf{K}_{mn} = [A_{mn}, \mathbf{d}], \ \mathbf{Q}_{mn} = [A_{mn}, \mathbf{m}]. \nabla$ and $\overleftarrow{\nabla}'$ operators act only on the first and second arguments of the Green's tensor; for example $\mathbf{G}(\mathbf{r}, \mathbf{r}_A, \omega) \times \overleftarrow{\nabla}' = \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) \times \overleftarrow{\nabla}' \Big|_{\mathbf{r}' = \mathbf{r}_A}$ Note that an electric dipole moment can produce a magnetic field and a magnetic dipole moment can create an electric field; these cross contributions are the relevant ones for the chiral part of the Casimir force.

In order to include the Lamb shifts and the dissipation of the molecular system we require the master equations for the populations $p_n(t) = \langle A_{nn}(t) \rangle$ and the coherences $\sigma_{nm}(t) = \langle A_{nm}(t) \rangle$, where the expectation value is taken over the field thermal state and the molecular internal state. The evolution of the populations are governed by the decay rates and the oscillations of the coherences are governed by the molecular transition frequencies. The electric field at the position of the molecule consists of two terms: the radiation reaction and the free field. As shown in the literature for a purely electric atom, the radiation reaction field gives rise to frequency shifts and spontaneous decay for molecule [23, 24]. We thus renormalise the field by splitting off the radiation reaction:

$$\left\langle \dot{A}_{mn} \right\rangle = \left[\mathrm{i}\tilde{\omega}_{mn} - \left(\Gamma_n + \Gamma_m\right)/2 \right] \left\langle A_{mn} \right\rangle \\ + \frac{\mathrm{i}}{\hbar} \left\langle \mathbf{K}_{mn} \cdot \mathbf{E}^{(0)} \left(\mathbf{r}_A\right) \right\rangle + \frac{\mathrm{i}}{\hbar} \left\langle \mathbf{Q}_{mn} \cdot \mathbf{B}^{(0)} \left(\mathbf{r}_A\right) \right\rangle$$
(4)

where $m \neq n$ and the expectation value is taken over the field thermal state and the molecular internal state. $\tilde{\omega}_{mn}$ are the Lamb-shifted molecular frequencies and Γ_k the decay rates, which have electric, magnetic and chiral contributions. Our model hence takes into account the dissipation of the molecular system; in this case there is only one channel of decay due to the interaction of the molecule with the bath of electromagnetic modes.

We integrate these equations of motion with respect to the time, starting from the initial time $t_0 = 0$ at which the molecule and the field are uncoupled, to obtain the free and induced flip operator and electromagnetic fields:

$$\langle A_{mn} (t) \rangle = \left\langle A_{mn}^{(0)} (t) \right\rangle + \frac{i}{\hbar} \int_{0}^{t} dt_{1} f_{mn} (t - t_{1}) \times \left\langle \mathbf{K}_{mn} (t_{1}) \cdot \mathbf{E}^{(0)} (\mathbf{r}_{A}, t_{1}) + \mathbf{Q}_{mn} (t_{1}) \cdot \mathbf{B}^{(0)} (\mathbf{r}_{A}, t_{1}) \right\rangle$$

$$\mathbf{E} (\mathbf{r}, \omega) = \mathbf{E}^{(0)} (\mathbf{r}, \omega) + \sum_{m,n} \int_{0}^{t} dt_{1} e^{-i\omega(t - t_{1})} A_{mn} (t_{1}) \times \left[\frac{i\mu_{0}}{\pi} \omega^{2} \mathrm{Im} \mathbf{G} (\mathbf{r}, \mathbf{r}_{A}, \omega) \cdot \mathbf{d}_{mn} \right. + \frac{\mu_{0}}{\pi} \omega \mathrm{Im} \mathbf{G} (\mathbf{r}, \mathbf{r}_{A}, \omega) \times \overleftarrow{\nabla}' \cdot \mathbf{m}_{mn} \right]$$

$$\mathbf{B} (\mathbf{r}, \omega) = \mathbf{B}^{(0)} (\mathbf{r}, \omega) + \sum_{m,n} \int_{0}^{t} dt_{1} e^{-i\omega(t - t_{1})} A_{mn} (t_{1}) \times \left[\frac{\mu_{0}}{\pi} \omega \nabla \times \mathrm{Im} \mathbf{G} (\mathbf{r}, \mathbf{r}_{A}, \omega) \cdot \mathbf{d}_{mn} \right. - \frac{i\mu_{0}}{\pi} \nabla \times \mathrm{Im} \mathbf{G} (\mathbf{r}, \mathbf{r}_{A}, \omega) \times \overleftarrow{\nabla}' \cdot \mathbf{m}_{mn} \right]$$

$$(5)$$

where \mathbf{d}_{mn} , \mathbf{m}_{mn} are the matrix elements of the electric and magnetic dipole operators between the states $|m\rangle$ and $|n\rangle$. We will consider time-reversal symmetric systems, where \mathbf{d}_{mn} is real and \mathbf{m}_{mn} purely imaginary [25] $(\mathbf{d}_{mn} = \mathbf{d}_{nm}, \mathbf{m}_{mn} = -\mathbf{m}_{nm})$. Furthermore, we have defined the function:

$$f_{mn}(t) = e^{[i\tilde{\omega}_{mn} - (\Gamma_n + \Gamma_m)/2]t}$$
(6)

The flip operator and the fields are the sum of the free terms, as they would be in absence of coupling, and induced terms. The molecule and field systems depend on their history because of their coupling.

III. DYNAMICAL CASIMIR-POLDER FORCE

We consider the electromagnetic force due to the interaction of a molecule exhibiting electric, magnetic and chiral polarisabilities with the body-assisted field. The field is in a thermal state with temperature T, while the molecule is in a generic internal state.

The CP force between the molecule and the bodi(es) is due to the exchange of a single photon: it is emitted, reflected by the bodi(es) and reabsorbed by the molecule (Fig. 1). The respective Feynman diagram must contain two interaction vertices which represent the emission and reabsorption of one photon. The electric contribution involves two electric-dipole interactions and the magnetic contribution involves two magnetic-dipole interactions. The chiral interaction involve one electric-dipole interaction and one magnetic-dipole interaction, in other words: the interaction must depend on cross terms with one electric dipole moment and one magnetic dipole moment.



FIG. 1. Casimir–Polder force: exchange of a single photon between the chiral molecule and the body.

The dynamical CP force for a fixed molecule is:

$$\mathbf{F} = \nabla \left\langle \mathbf{d}(t) \cdot \mathbf{E}(\mathbf{r}, t) \right\rangle |_{\mathbf{r} = \mathbf{r}_{A}} + \nabla \left\langle \mathbf{m}(t) \cdot \mathbf{B}(\mathbf{r}, t) \right\rangle |_{\mathbf{r} = \mathbf{r}_{A}}$$
(7)

where all operators are obtained by solving the Heisenberg equations and the expectation value is taken over the thermal field state and the internal molecular state. We can express the electric field in terms of its free part and the source field due to the molecule (see Eq. (5)):

$$\mathbf{F}(t) = \int_{0}^{\infty} d\omega \sum_{m,n} \nabla \left\langle A_{mn}\left(t\right) \mathbf{d}_{mn} \cdot \mathbf{E}^{(0)}\left(\mathbf{r},\omega,t\right) \right\rangle \Big|_{\mathbf{r}=\mathbf{r}_{A}} \\ + \int_{0}^{\infty} d\omega \sum_{m,n} \nabla \left\langle A_{mn}\left(t\right) \mathbf{m}_{mn} \cdot \mathbf{B}^{(0)}\left(\mathbf{r},\omega,t\right) \right\rangle \Big|_{\mathbf{r}=\mathbf{r}_{A}} \\ + \frac{i\mu_{0}}{\pi} \sum_{m,n} \sum_{p,q} \int_{0}^{\infty} d\omega \int_{0}^{t} dt_{1} e^{-i\omega(t-t_{1})} \left\langle A_{mn}\left(t\right) A_{pq}\left(t_{1}\right) \right\rangle \\ \times \nabla \left\{ \omega^{2} \mathbf{d}_{mn} \cdot \mathrm{Im}\mathbf{G}\left(\mathbf{r}_{A},\mathbf{r}_{A},\omega\right) \times \mathbf{\nabla}^{\prime} \cdot \mathbf{m}_{pq} \\ - \mathbf{m}_{mn} \cdot \nabla \times \mathrm{Im}\mathbf{G}\left(\mathbf{r}_{A},\mathbf{r}_{A},\omega\right) \times \mathbf{\nabla}^{\prime} \cdot \mathbf{m}_{pq} \\ - i\omega \mathbf{d}_{mn} \cdot \mathrm{Im}\mathbf{G}\left(\mathbf{r}_{A},\mathbf{r}_{A},\omega\right) \times \mathbf{\nabla}^{\prime} \cdot \mathbf{m}_{pq} \\ - i\omega \mathbf{m}_{mn} \cdot \nabla \times \mathrm{Im}\mathbf{G}\left(\mathbf{r}_{A},\mathbf{r}_{A},\omega\right) \cdot \mathbf{d}_{pq} \right\} + \mathrm{c.c.} \quad (8)$$

As already mentioned, ∇ and $\overleftarrow{\nabla}'$ operators act only on the first and second arguments of the Green's tensor, respectively:

$$\nabla \mathbf{G} (\mathbf{r}_{A}, \mathbf{r}_{A}) = \nabla \mathbf{G} (\mathbf{r}, \mathbf{r}_{A})|_{\mathbf{r}=\mathbf{r}_{A}}$$
$$\nabla' \mathbf{G} (\mathbf{r}_{A}, \mathbf{r}_{A}) = \nabla' \mathbf{G} (\mathbf{r}_{A}, \mathbf{r}')|_{\mathbf{r}'=\mathbf{r}_{A}}$$
(9)

In the first two terms in (8), we use the dynamical equations (5) for the flip operator:

$$\begin{aligned} \mathbf{F}(t) &= \frac{\mathrm{i}}{\hbar} \int_{0}^{\infty} \mathrm{d}\omega \int_{0}^{\infty} \mathrm{d}\omega' \sum_{m,n} \int_{0}^{t} \mathrm{d}t_{1} f_{mn} \left(t - t_{1}\right) \\ &\times \nabla \left\langle \left[\mathbf{E}^{(0)\dagger} \left(\mathbf{r}_{A}, \omega', t_{1}\right) \cdot \mathbf{K}_{mn} \left(t_{1}\right) \right. \\ &+ \mathbf{B}^{(0)\dagger} \left(\mathbf{r}_{A}, \omega', t_{1}\right) \cdot \mathbf{Q}_{mn} \left(t_{1}\right) \right] \right. \\ &\times \left[\mathbf{d}_{mn} \cdot \mathbf{E}^{(0)} \left(\mathbf{r}, \omega, t\right) + \mathbf{m}_{mn} \cdot \mathbf{B}^{(0)} \left(\mathbf{r}, \omega, t\right) \right] \right\rangle \Big|_{\mathbf{r} = \mathbf{r}_{A}} \\ &+ \frac{\mathrm{i}\mu_{0}}{\pi} \sum_{m,n} \sum_{p,q} \int_{0}^{\infty} \mathrm{d}\omega \int_{0}^{t} \mathrm{d}t_{1} \mathrm{e}^{-\mathrm{i}\omega(t - t_{1})} \left\langle A_{mn} \left(t\right) A_{pq} \left(t_{1}\right) \right\rangle \\ &\quad \times \nabla \left\{ \omega^{2} \mathbf{d}_{mn} \cdot \mathrm{Im} \mathbf{G} \left(\mathbf{r}_{A}, \mathbf{r}_{A}, \omega\right) \times \mathbf{\nabla}' \cdot \mathbf{m}_{pq} \\ &- \mathbf{m}_{mn} \cdot \nabla \times \mathrm{Im} \mathbf{G} \left(\mathbf{r}_{A}, \mathbf{r}_{A}, \omega\right) \times \mathbf{\nabla}' \cdot \mathbf{m}_{pq} \\ &- \mathrm{i}\omega \mathbf{d}_{mn} \cdot \mathrm{Im} \mathbf{G} \left(\mathbf{r}_{A}, \mathbf{r}_{A}, \omega\right) \cdot \mathbf{d}_{pq} \right\} + \mathrm{c.c.} \quad (10) \end{aligned}$$

The thermal expectation value of two positive-frequency electromagnetic fields is zero.

Next, we use the known formula for the field fluctua-

tions [15]:

$$\left\langle \mathbf{E}^{(0)\dagger}\left(\mathbf{r},\omega\right)\mathbf{E}^{(0)}\left(\mathbf{r}',\omega'\right)\right\rangle = \frac{\hbar\mu_{0}}{\pi}\operatorname{Im}\mathbf{G}\left(\mathbf{r},\mathbf{r}',\omega\right)\omega^{2}\delta\left(\omega-\omega'\right)n\left(\omega\right) \left\langle \mathbf{E}^{(0)\dagger}\left(\mathbf{r},\omega\right)\mathbf{B}^{(0)}\left(\mathbf{r}',\omega'\right)\right\rangle = \frac{i\hbar\mu_{0}}{\pi}\operatorname{Im}\mathbf{G}\left(\mathbf{r},\mathbf{r}',\omega\right)\times\overleftarrow{\nabla}'\omega\delta\left(\omega-\omega'\right)n\left(\omega\right) \left\langle \mathbf{B}^{(0)\dagger}\left(\mathbf{r},\omega\right)\mathbf{E}^{(0)}\left(\mathbf{r}',\omega'\right)\right\rangle = \frac{i\hbar\mu_{0}}{\pi}\nabla\times\operatorname{Im}\mathbf{G}\left(\mathbf{r},\mathbf{r}',\omega\right)\omega\delta\left(\omega-\omega'\right)n\left(\omega\right) \left\langle \mathbf{B}^{(0)\dagger}\left(\mathbf{r},\omega\right)\mathbf{B}^{(0)}\left(\mathbf{r}',\omega'\right)\right\rangle = -\frac{\hbar\mu_{0}}{\pi}\nabla\times\operatorname{Im}\mathbf{G}\left(\mathbf{r},\mathbf{r}',\omega\right)\times\overleftarrow{\nabla}'\delta\left(\omega-\omega'\right)n\left(\omega\right)$$
(11)

where $n(\omega)$ is the Bose-Einstein distribution:

$$n(\omega) = \frac{1}{\mathrm{e}^{\hbar\omega/k_BT} - 1} \,. \tag{12}$$

We also perform the expectation value on the internal molecular state, which is an incoherent superposition of energy eigenstates $|n\rangle$, with probabilities p_n . Furthermore, the two-time correlation function can be simplified with the Lax regression theorem [26, 27] $(t_1 \leq t)$:

$$\langle A_{mn}(t) A_{pq}(t_1) \rangle = f_{mn}(t-t_1) \langle A_{mn}(t_1) A_{pq}(t_1) \rangle = f_{mn}(t-t_1) \delta_{np} \langle A_{mq}(t_1) \rangle$$
(13)

Approximating $\langle A_{mn}(t_1) \rangle \simeq e^{i\tilde{\omega}_{mn}(t_1-t)} \langle A_{mn}(t) \rangle$, the CP force is a weighted sum of the CP forces associated with each eigenstate $\mathbf{F}(t) = \sum_{n} p_n(t) \mathbf{F}_n(t)$:

$$\mathbf{F}_{n}(t) = \frac{\mathrm{i}\mu_{0}}{\pi} \int_{0}^{\infty} \mathrm{d}\omega \sum_{k} \int_{0}^{t} \mathrm{d}t_{1} \mathrm{e}^{-\mathrm{i}\omega(t-t_{1})}$$

$$\times \{f_{nk} (t-t_{1}) [1+n(\omega)] - f_{kn} (t-t_{1}) n(\omega)\}$$

$$\times \nabla \{\omega^{2} \mathbf{d}_{nk} \cdot \mathrm{Im}\mathbf{G} (\mathbf{r}_{A}, \mathbf{r}_{A}, \omega) \cdot \mathbf{d}_{kn}$$

$$- \mathbf{m}_{nk} \cdot \nabla \times \mathrm{Im}\mathbf{G} (\mathbf{r}_{A}, \mathbf{r}_{A}, \omega) \times \overleftarrow{\nabla}' \cdot \mathbf{m}_{kn}$$

$$-2\mathrm{i}\omega \mathbf{m}_{nk} \cdot \nabla \times \mathrm{Im}\mathbf{G} (\mathbf{r}_{A}, \mathbf{r}_{A}, \omega) \cdot \mathbf{d}_{kn}\} + \mathrm{c.c.}$$

where $p_n(t) = \langle A_{nn}(t) \rangle$ is the population of energy-state $|n\rangle$. To obtain this expression we have used the Green tensor reciprocity theorem $\mathbf{G}^T(\mathbf{r},\mathbf{r}') = \mathbf{G}(\mathbf{r}',\mathbf{r})$, and for the chiral part the property $\left[\mathbf{G}(\mathbf{r}_A,\mathbf{r}_A,\omega)\times\overleftarrow{\nabla}'\right]^T = -\nabla\times\mathbf{G}(\mathbf{r}_A,\mathbf{r}_A,\omega)$. The term proportional to the Bose-Einstein distribution describes the interaction between the molecule and the thermal field, while the term independent of n describes the interaction with the vacuum field.

Now we introduce ∇_A which acts on both arguments of the Green tensor. Exploiting Onsager reciprocity, the relation

$$\nabla_{A}\mathbf{G}(\mathbf{r}_{A},\mathbf{r}_{A})$$

$$= \nabla\mathbf{G}(\mathbf{r},\mathbf{r}_{A})|_{\mathbf{r}=\mathbf{r}_{A}} + \nabla'\mathbf{G}(\mathbf{r}_{A},\mathbf{r}')|_{\mathbf{r}'=\mathbf{r}_{A}}$$

$$= \nabla\mathbf{G}(\mathbf{r}_{A},\mathbf{r}_{A}) + \nabla'\mathbf{G}(\mathbf{r}_{A},\mathbf{r}_{A})$$

$$= \nabla\mathbf{G}(\mathbf{r}_{A},\mathbf{r}_{A}) + \nabla\mathbf{G}^{T}(\mathbf{r}_{A},\mathbf{r}_{A}) \quad (14)$$

holds. For a time-reversal symmetric molecule, we can hence make the replacement:

$$\nabla \mathbf{G}(\mathbf{r}_A, \mathbf{r}_A, \omega) \to \frac{1}{2} \nabla_A \mathbf{G}(\mathbf{r}_A, \mathbf{r}_A, \omega)$$
 (15)

After performing the time-integrals we obtain:

$$\mathbf{F}(t) = \sum_{n} p_{n}(t) \left[\mathbf{F}_{n}^{e}(t) + \mathbf{F}_{n}^{m}(t) + \mathbf{F}_{n}^{c}(t) \right],$$

$$\mathbf{F}_{n}^{e}(t) = \frac{\mu_{0}}{2\pi} \int_{0}^{\infty} d\omega \omega^{2} \sum_{k} \Psi_{kn}(\omega, t)$$

$$\times \nabla_{A} \mathbf{d}_{nk} \text{Im} \mathbf{G} \left(\mathbf{r}_{A}, \mathbf{r}_{A}, \omega \right) \mathbf{d}_{kn},$$

$$\mathbf{F}_{n}^{m}(t) = -\frac{\mu_{0}}{2\pi} \int_{0}^{\infty} d\omega \sum_{k} \Psi_{kn}(\omega, t)$$

$$\times \nabla_{A} \mathbf{m}_{nk} \nabla \times \text{Im} \mathbf{G} \left(\mathbf{r}_{A}, \mathbf{r}_{A}, \omega \right) \times \overleftarrow{\nabla}' \mathbf{m}_{kn},$$

$$\mathbf{F}_{n}^{c}(t) = -\frac{i\mu_{0}}{\pi} \int_{0}^{\infty} d\omega \omega \sum_{k} \Psi_{kn}(\omega, t)$$

$$\times \nabla_{A} \mathbf{m}_{nk} \nabla \times \text{Im} \mathbf{G} \left(\mathbf{r}_{A}, \mathbf{r}_{A}, \omega \right) \mathbf{d}_{kn}$$
(16)

where

$$\Psi_{kn}(\omega,t) = \frac{1 - e^{-it\left(\omega + \omega_{kn}^{(-)}\right)}}{\omega + \omega_{kn}^{(-)}} \left[1 + n\left(\omega\right)\right] - \frac{1 - e^{-it\left(\omega - \omega_{kn}^{(+)}\right)}}{\omega - \omega_{kn}^{(+)}} n\left(\omega\right) + \text{c.c.} \quad (17)$$

and $\omega_{kn}^{(\pm)} = \tilde{\omega}_{kn} \pm i (\Gamma_n + \Gamma_k) / 2$. As explained before, for time-reversal symmetric systems, the electric dipole elements are real and the magnetic dipole elements purely imaginary. We have separated the electric, magnetic and chiral contributions: electric contribution contains two electric dipole moments, the magnetic contribution two magnetic dipole moments and chiral contribution contains cross terms with one electric dipole moment and one magnetic dipole moment.

We observe that the force depends on time in two ways: firstly, the populations of the internal molecular states may depend on time. For example, a molecule initially prepared in some excited state will unavoidably decay to the ground state, so the population of the excited state is one for short times but zero for large times. The time scale of this population-induced dynamics of the force is set by the life times $\tau_n = 1/\Gamma_n$ of the initially populated states. For a ground-state molecule the populations of the energy levels are constant in time and there is no population-induced dynamics.

The time-dependent exponentials on the other hand describe the dynamical self-dressing of the molecule which is the focus of this work. The self-dressing dynamics operates on the much shorter time scales of the order of the inverse molecular transition frequencies $1/\omega_{nk}$. The dynamical self-dressing has been considered for a single non-absorbing electric molecule in front a plate [19]; our approach is generalized for finite temperature, arbitrary geometry of the body and it accounts for molecular absorption.

For times much larger than $1/\omega_{nk}$, the exponential function is rapidly oscillating and averages to zero. The electric part of the CP force then converges to the value obtained in the literature with a dynamical approach where the time-dependence is solely due to populationinduced dynamics [23, 28]. Our new results hence generalise the previous dynamical approach to include the self-dressing of the molecule as well as the magnetic and the chiral parts of the interactions. The static limit of our result for the chiral contribution extends previous results from time-independent perturbation theory to finite temperature and absorbing molecules [15].

As a simple example, we consider an isotropic nonabsorbing molecule. The electric, magnetic and chiral parts of the dynamical Casimir–Polder interaction are:

$$\mathbf{F}_{n}(t) = \mathbf{F}_{n}^{e}(t) + \mathbf{F}_{n}^{m}(t) + \mathbf{F}_{n}^{c}(t)$$

$$\mathbf{F}_{n}^{e}(t) = \frac{\mu_{0}}{3\pi} \int_{0}^{\infty} d\omega \omega^{2} \sum_{k} \mathbf{d}_{nk} \cdot \mathbf{d}_{kn} \Psi_{kn}'(\omega, t)$$

$$\times \nabla_{A} \operatorname{Tr} \left\{ \operatorname{Im} \mathbf{G} \left(\mathbf{r}_{A}, \mathbf{r}_{A}, \omega \right) \right\},$$

$$\mathbf{F}_{n}^{m}(t) = -\frac{\mu_{0}}{3\pi} \int_{0}^{\infty} d\omega \sum_{k} \mathbf{m}_{nk} \cdot \mathbf{m}_{kn} \Psi_{kn}'(\omega, t)$$

$$\times \nabla_{A} \operatorname{Tr} \left\{ \nabla \times \operatorname{Im} \mathbf{G} \left(\mathbf{r}_{A}, \mathbf{r}_{A}, \omega \right) \times \overleftarrow{\nabla}' \right\},$$

$$\mathbf{F}_{n}^{c}(t) = -\frac{2\mu_{0}}{3\pi} \int_{0}^{\infty} d\omega \omega \sum_{k} R_{nk} \Psi_{kn}'(\omega, t)$$

$$\times \nabla_{A} \operatorname{Tr} \left\{ \nabla \times \operatorname{Im} \mathbf{G} \left(\mathbf{r}_{A}, \mathbf{r}_{A}, \omega \right) \right\}$$
(18)

where

$$\Psi'_{kn}(\omega, t) = \frac{1 + n(\omega)}{\omega_{kn} + \omega} \left(1 - \cos\left[\left(\omega_{kn} + \omega\right)t\right]\right) \\ + \frac{n(\omega)}{\omega_{kn} - \omega} \left(1 - \cos\left[\left(\omega_{kn} - \omega\right)t\right]\right), \quad (19)$$

Tr is the trace, $R_{nk} = \text{Im} (\mathbf{d}_{nk} \cdot \mathbf{m}_{kn})$ is the rotatory strength and ω_{kn} the transition frequency between the state $|k\rangle$ and $|n\rangle$.

If either the medium $(\operatorname{Tr} \{ \nabla \times \operatorname{Im} \mathbf{G} (\mathbf{r}_A, \mathbf{r}_A, \omega) \} = 0)$, or

the particle $(R_{nk} = 0)$ is achiral there will be no chiral component to the Casimir–Polder potential. This can be thought of as an application of to the Curie dissymmetry principle (originally formulated for crystal symmetries): the CP potential cannot distinguish between molecules of different handedness if the medium does not possess chiral properties itself.

Under reflection, the electric dipole moment changes sign, while the magnetic dipole moment does not. The electric and magnetic parts of the dynamical interaction hence do not change if the molecule is substituted with its enantiomer (mirror image), but the chiral part of the CP force changes sign. This shows the discriminatory effect for the chiral part of the dynamical interaction.

IV. CHIRAL MOLECULE IN FRONT A PERFECT MIRROR

The interaction between a ground-state electric molecule and a perfectly conducting electric plate at zerotemperature has been investigated in the literature [19]; the results can be recovered with our model but we will not focus on this point here. We consider instead the interaction between a ground-state chiral molecule and and a perfectly reflecting chiral plate at zero temperature, $n(\omega) = 0$. As the population of the ground state is constant in time, the only dynamics of the Casimir– Polder force arises due to self-dressing.

The Green's tensor of the perfectly reflecting chiral plate is known, and it depends only in the distance d between the molecule and the mirror [15, 29]:

$$\frac{\partial}{\partial d} \left\{ \omega \nabla \times \operatorname{Im} \mathbf{G} \left(\mathbf{r}_A, \mathbf{r}_A, \omega \right) \right\} = \\ \pm \frac{3c}{8\pi d^4} \left[\cos x + x \sin x - \frac{1}{3} x^2 \cos x \right]_{x = 2d\omega/c}$$
(20)

where the sign + or - refers to plates of positive and negative chirality, respectively. Note that the trace of the Green tensor scales differently for small and larges distances leading to different dependences of the force on the distance.

After inserting this expression into Eq. (18), we next need to perform the frequency integrals for the three terms in the above Eq. (20). This task can be simplified considerably by expressing the Green's tensor in terms of a differential operator:

$$\frac{\partial}{\partial d} \left\{ \omega \nabla \times \operatorname{Im} \mathbf{G} \left(\mathbf{r}_{A}, \mathbf{r}_{A}, \omega \right) \right\} = \\ \pm \frac{3c}{8\pi d^{4}} \lim_{m \to 1} \left[1 - \frac{\partial}{\partial m} + \frac{1}{3} \frac{\partial^{2}}{\partial m^{2}} \right] \cos\left(mx\right)|_{x = 2d\omega/c}$$
(21)

Inserting the Green's tensor in this form, the chiral in-

teraction reads:

$$\mathbf{F}^{c} = \mp \frac{1}{4\pi^{2}\varepsilon_{0}cd^{4}} \lim_{m \to 1} \left[1 - \frac{\partial}{\partial m} + \frac{1}{3}\frac{\partial^{2}}{\partial m^{2}} \right]$$
$$\times \sum_{k} R_{0k} \int_{0}^{\infty} \mathrm{d}x \frac{\cos\left(mx\right)}{x + x_{k}} \left(1 - \cos\left[\left(x + x_{k}\right)a\right] \right) \hat{d} \quad (22)$$

where $x = 2d\omega/c$, $x_k = 2d\omega_k/c$ and a = ct/(2d) and $\hat{d} = \mathbf{d}/d$.

A. Stationary case: large times

For times much larger than $1/\omega_k$, the cosine function oscillates rapidly and its contribution vanishes; this situation corresponds to a totally dressed molecule.

We introduce the auxiliary functions, for m, y > 0:

$$F(m, y) = \int_{0}^{\infty} dx \frac{\sin(mx)}{x+y}$$

= sin (my) Ci (my) - cos (my) [Si (my) - $\frac{\pi}{2}$]
G (m, y) = $\int_{0}^{\infty} dx \frac{\cos(mx)}{x+y}$
= - cos (my) Ci (my) - sin (my) [Si (my) - $\frac{\pi}{2}$]
(23)

where Si and Ci are the sine and cosine integral functions. For large times the CP force converges to the following static force:

$$\mathbf{F}_{t \to \infty}^{c} = \mp \frac{1}{4\pi^{2}\varepsilon_{0}cd^{4}} \sum_{k} R_{0k}$$

$$\times \lim_{m \to 1} \left[1 - \frac{\partial}{\partial m} + \frac{1}{3}\frac{\partial^{2}}{\partial m^{2}} \right] \mathbf{G}(m, x_{k}) \hat{d}$$

$$= \mp \frac{1}{3\pi^{2}\varepsilon_{0}cd^{4}} \sum_{k} R_{0k}$$

$$\times \left[1 - 2\operatorname{Ci}\left(2k_{k}d\right) f\left(k_{k}d\right) + \left(2\operatorname{Si}\left(2k_{k}d\right) - \pi\right) g\left(k_{k}d\right) \right] \hat{d}$$

where $k_k = \frac{\omega_k}{c}$ is the molecular wave number and we have introduced the auxiliary functions:

$$f(x) = \frac{3x}{4} \sin(2x) + \left(\frac{3}{8} - \frac{x^2}{2}\right) \cos(2x)$$
$$g(x) = \frac{3x}{4} \cos(2x) - \left(\frac{3}{8} - \frac{x^2}{2}\right) \sin(2x)$$
(24)

This is an alternative, slightly more explicit form for the result known in the literature [15, 29].

As an example of a chiral molecule, consider dimethyl disulphide $(CH_3)_2S_2$. The dipole and rotatory strengths for each transition have been numerically calculated for

various orientations [30]. As an example, we have chosen the first transition when the orientation between the two $CH_3 - S - S$ planes is 90°. The transition frequency between the excited state and the ground state is $\omega_{10} = 9.17 \cdot 10^{15}$ Hz, the square of the dipole moment $|\mathbf{d}_{01}|^2 = 8.264 \cdot 10^{-60} (\text{Cm})^2$ and the rotatory strength is $R_{10} = 3.328 \cdot 10^{-64} \text{C}^2 \text{m}^3 \text{s}^{-1}$. Fig. 2 shows the chiral Casimir–Polder force for a ground-state dimethyl disulphide molecule above a perfect mirror of negative chirality. The stationary chiral CP force between the ground-state molecule and the medium is repulsive due to the chosen opposite chiralities of molecule and mirror. This differs from the CP interaction between an electric molecule and a perfectly conducting electric plate, which is attractive [2, 19, 22].



FIG. 2. Stationary chiral Casimir–Polder interaction between a ground-state dimethyl disulphide and a perfect mirror of negative chirality.

The distance-dependence of the chiral CP force can be reduced to simple power laws in the retarded and nonretarded limits. In the non-retarded limit $d \ll \lambda_k$ or equivalently $x_k \ll 1$, we may approximate $G(m, x_k) \rightarrow$ $-\gamma - \log(mx_k)$ where γ is the Euler–Mascheroni constant. The force is then [15, 29]:

$$\mathbf{F}_{non-ret} = \pm \frac{1}{4\pi^2 \varepsilon_0 c d^4} \sum_k R_{0k} \log\left(\frac{\omega_k d}{c}\right) \hat{d} \qquad (25)$$

In the retarded limit $d \gg \lambda_k$ or equivalently $x_k \gg 1$, we have $G(m, x_k) \to \frac{1}{(mx_k)^2}$ and the force is [15, 29]:

$$\mathbf{F}_{ret} = \mp \frac{5c}{16\pi^2 \varepsilon_0 d^6} \sum_k \frac{R_{0k}}{\omega_k^2} \hat{d}$$
(26)

As expected, the retarded interaction decreases more rapidly due to the finite velocity of the light: during the time in which the virtual photon has been exchanged, the molecule will evolve. This associated loss of correlation leads to a more rapidly decreasing force.

Due to the unusual $\log\left(\frac{\omega_k d}{c}\right)/d^4$ dependence of the force in the non-retarded limit, the chiral potential grows more rapidly than the electric and magnetic potentials when approaching the surface.

The chiral force changes sign if the molecule is substitute with its entaniomer, or when the plate of negative chirality is substituted with one of negative chirality. This discriminatory effect is also observed in the dynamic case, which we will consider in the next section.

B. Dynamical case

We now consider the dynamical situation in which the interaction with the perfect chiral plate starts at the initial time $t_0 = 0$ and we ask for the dynamical Casimir–Polder force between the chiral molecule and the mirror. In this case, the bare molecular state is not an eigenstate of the total Hamiltonian, and thus it evolves in time (dynamical self-dressing), yielding a time-dependent force between the mirror and the molecule.

To evaluate the force, we use the trigonometric relation

$$\cos(mx) (1 - \cos[(x + x_k) a]) = \cos(mx) - \frac{\cos(ax_k)}{2} \{\cos[(m + a) x] + \cos[(m - a) x]\} + \frac{\sin(ax_k)}{2} \{\sin[(m + a) x] - \sin[(m - a) x]\}$$

The force has two different expressions before and after the back-reaction time (t = 2d/c), which is the time needed for light emitted by the atom to be reflected by the mirror and return to the molecule. For t < 2d/c and t > 2d/c the chiral dynamical CP force is:

$$\mathbf{F}_{t<2d/c}^{c} = \mp \frac{1}{4\pi^{2}\varepsilon_{0}cd^{4}} \sum_{k} R_{0k} \lim_{m \to 1} \left[1 - \frac{\partial}{\partial m} + \frac{1}{3} \frac{\partial^{2}}{\partial m^{2}} \right] \left\{ \mathbf{G}(m, x_{k}) + \frac{-\frac{\cos\left(ax_{k}\right)}{2} \left[\mathbf{G}(m+a, x_{k}) + \mathbf{G}(m-a, x_{k}) \right] + \frac{\sin\left(ax_{k}\right)}{2} \left[\mathbf{F}(m+a, x_{k}) - \mathbf{F}(m-a, x_{k}) \right] \right\} \hat{d} \\ = \mp \frac{1}{3\pi^{2}\varepsilon_{0}cd^{4}} \sum_{k} R_{0k} \left[1 - \frac{8d^{4}\cos\left(\omega_{k}t\right)}{\left(c^{2}t^{2} - 4d^{2}\right)^{2}} + \frac{2d^{2}\cos\left(\omega_{k}t\right) + d^{2}\omega_{k}t\sin\left(\omega_{k}t\right)}{c^{2}t^{2} - 4d^{2}} \right] \\ - \left[2\operatorname{Ci}\left(2k_{k}d\right) - \operatorname{Ci}\left(2k_{k}d - \omega_{k}t\right) - \operatorname{Ci}\left(2k_{k}d + \omega_{k}t\right) \right] f\left(k_{k}d\right) \\ + \left[2\operatorname{Si}\left(2k_{k}d\right) - \operatorname{Si}\left(2k_{k}d - \omega_{k}t\right) - \operatorname{Si}\left(2k_{k}d + \omega_{k}t\right) \right] g\left(k_{k}d\right) \right] \hat{d}$$

$$(27)$$

$$\mathbf{F}_{t>2d/c}^{c} = \mp \frac{1}{4\pi^{2}\varepsilon_{0}cd^{4}} \sum_{k} R_{0k} \lim_{m \to 1} \left[1 - \frac{\partial}{\partial m} + \frac{1}{3} \frac{\partial^{2}}{\partial m^{2}} \right] \left\{ \mathbf{G}\left(m, x_{k}\right) + \frac{1}{2} \frac{\partial^{2}}{\partial m^{2}} \right\} \left[\mathbf{G}\left(m, x_{k}\right) + \frac{1}{2} \frac{\partial^{2}}{\partial m^{2}} \right] \left\{ \mathbf{G}\left(m, x_{k}\right) + \frac{1}{2} \frac{\partial^{2}}{\partial m^{2}} \left[\mathbf{G}\left(m, x_{k}\right) + \frac{1}{2} \frac{\partial^{2}}{\partial m^{2}} \right] \left\{ \mathbf{G}\left(m, x_{k}\right) + \frac{1}{2} \frac{\partial^{2}}{\partial m^{2}} \right] \left\{ \mathbf{G}\left(m, x_{k}\right) + \frac{1}{2} \frac{\partial^{2}}{\partial m^{2}} \right\} \left[\mathbf{G}\left(m, x_{k}\right) + \frac{1}{2} \frac{\partial^{2}}{\partial m^{2}} \right] \left\{ \mathbf{G}\left(m, x_{k}\right) + \frac{1}{2} \frac{\partial^{2}}{\partial m^{2}} \right\} \left\{ \mathbf{G}\left(m, x_{k}\right) + \frac{1}{2} \frac{\partial^{2}}{\partial m^{2}} \left\{ \mathbf{G}\left(m, x_{k}\right) + \frac{1}{2} \frac{\partial^{2}}{\partial m^{2}} \right\} \left\{ \mathbf{G}\left(m, x_{k}\right) + \frac{1}{2} \frac{\partial^{2}}{\partial m^{2}} \left\{ \mathbf{G}\left(m, x_{k}\right) + \frac{1}{2} \frac{\partial^{2}}{\partial m^{2}} \right\} \left\{ \mathbf{G}\left(m, x_{k}\right) + \frac{1}{2} \frac{\partial^{2}}{\partial m^{2}} \left\{ \mathbf{G}\left(m, x_{k}\right) + \frac{1}{2} \frac{\partial^{2}}{\partial m^{2}} \left\{ \mathbf{G}\left(m, x_{k}\right) + \frac{1}{2} \frac{\partial^{2}}{\partial m^{2}} \right\} \left\{ \mathbf{G}\left(m, x_{k}\right) - \frac{1}{2} \frac{\partial^{2}}{\partial m^{2}} \left\{ \mathbf{G}\left(m, x_{k}\right) + \frac{1}{2} \frac{\partial^{2}}{\partial m^{2}$$

where the functions f, g are defined by Eq. (24). It is easy to show that $\mathbf{F} \to 0$ for $t \to 0$; this is due to the fact that we switch on the interaction at the initial time $t_0 = 0$.

For subsequent times, the force increases exhibiting an oscillatory behaviour in time. Depending on the time, the force can be attractive and repulsive for a given distance, contrary to the static case where it has a definite sign. This is illustrated in Fig. 3, where we display the chiral CP force at fixed distance from the mirror before the back-reaction time.



FIG. 3. Chiral dynamical Casimir–Polder interaction between an ground-state dimethyl disulphide and a negative perfect chiral medium for $d = 0.1 \mu m$ and t < 2d/c = 0.67 fs.

For large times, the force converges to the static force; this corresponds to a totally dressed molecule. Fig. 4 shows the dynamics of the chiral force after the backreaction.



FIG. 4. Chiral dynamical Casimir–Polder interaction between an ground-state dimethyl disulphide and a negative perfect chiral medium for $d = 0.1 \,\mu\text{m}$ and t > 2d/c = 0.67 fs.

To interpret our results, recall that the CP force is due to the exchange of one virtual photon between the molecule and the mirror. Different expressions for the force are needed before and after the backreaction time because the photon needs a finite time in order to be reflected and absorbed by the molecule. Note that the force is non-vanishing even before the backreaction time, because the molecule interacts with the field modes which incorporate the presence of the conducting wall and hence instantaneously feels the presence of the mirror. This is because we are evaluating the force on the atom, which responds to the local field at its position and thus it is immediately influenced by a change of the atom's physical parameters. We expect that, if the force on the conducting wall were evaluated, it would be influenced by a change of the atomic parameters (or by a sudden switching on of the atom-field interaction) only after the causality time t = d/c.

The force is divergent on the light cone t = 2d/c, because in the frequency-integral we include arbitrarily large frequencies: this divergence is not surprising, being due to the assumption of a point-like molecule (dipole approximation) and to the idealised nature of the material. A real material is transparent for large frequencies, providing a natural cut-off to regularize the integral; moreover, also the inclusion of a finite size of the atom/molecule would provide a natural ultraviolet cutoff given by the appropriate atomic form factor.

V. CONCLUSIONS

Using a dynamical approach, we have obtained the electric, magnetic and the chiral parts of the timedependent Casimir–Polder interaction between an initially bare chiral molecule and a body at finite temperature, the molecule initially being prepared in a generic internal state. The force depends on time because the populations of the excited states of the molecule depend on time (population-induced dynamics), but also because of the initial boundary condition (self-dressing induced dynamics).

As an example we have considered the particular case of the interaction between an initially bare ground-state chiral molecule and perfectly reflecting chiral plate at zero temperature. Here, the force is time-dependent only because of self-dressing. The dynamical CP can be attractive or repulsive depending on time, contrary to the static case where it has a definite sign for a given distance.

The dynamical interaction is due to the exchange of one virtual photon between the chiral molecule and the mirror. A characteristic time scale of the dynamical CP force is the time taken by the virtual photon to be emitted by the molecule, reflected by the mirror, and reabsorbed by the molecule (back-reaction time). The dynamical interaction oscillates in time and the scale of these oscillations is related to the molecular transition frequency. The dynamical effect we have considered could in principle be measured by switching on the interaction between the molecule and the field at the initial time $t_0 = 0$. Even if this is an idealized situation, it could be approximated by the more realistic case of a rapid change of some parameter characterizing the atom-field interaction (strength and/or orientation of the atomic dipole moments, atomic transition frequency by Stark shift, for example) or putting the atom at some distance from the macroscopic body [31]. Another possibility to obtain a dynamical effect could be introducing the mirror at $t_0 = 0$; however, because in our formalism the presence of the mirror is included in the boundary conditions and not in the system's dynamics, this would require a different approach based on a transformation of field operators and modes relating old and new ones (i.e. before and after switching on the mirror), similarly to the dynamical Casimir effect. The use of chiral Rydberg atoms, which have low transition frequencies and large polarizabilities, could be a simpler system to measure the dynamical Casimir force, because in this case the dynamical force evolves on longer timescales [32] ($\tau = 10^{-9}s$).

We have shown that the chiral Casimir–Polder interaction shows a discriminatory effect because it changes sign if the molecule is substituted by its enantiomer and the dynamical force can hence allow us to distinguish different enantiomers.

We finally remark that in our approach the medium is considered macroscopically with the electromagnetic Green tensor. Our model can be generalized to different molecular internal states and different geometries in which the Green's tensor is known.

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