Transfer of linear momentum from the quantum vacuum to a magnetochiral molecule

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Abstract

In a recent publication [1] we have shown using a QED approach that, in the presence of a magnetic field, the quantum vacuum coupled to a chiral molecule provides a kinetic momentum directed along the magnetic field. Here we explain the physical mechanisms which operate in the transfer of momentum from the vacuum to the molecule. We show that the variation of the molecular kinetic energy originates from the magnetic energy associated with the vacuum correction to the magnetization of the molecule. We carry out a semiclassical calculation of the vacuum momentum and compare the result with the QED calculation.

Keywords: Casimir momentum, quantum electrodynamics, vacuum symmetries

(Some figures may appear in colour only in the online journal)

1. Introduction

It is well known that the quantum fluctuations of the electromagnetic (EM) field coupled to electric charges generate an observable interaction energy [2–4]. The fluctuations which mediate the self-interaction of electrons bound to atomic nuclei give rise to the Lamb shift of atomic levels; the fluctuations which mediate the interaction between nearby molecules generate van-der-Waals energies; and finally the fluctuations between macroscopic dielectrics generate the Casimir energy. Direct observation of these energies is possible by spectroscopy, atomic interferometry or nanomechanical means [5–8].

Less well known is the fact that other observable quantities, functions of the EM field, can be influenced by quantum fluctuations under certain symmetry conditions. That is, when the time-space symmetries of the medium to which the fluctuations couple are compatible with the symmetries of some observable operator, the expectation value of that operator in the vacuum state of the system medium-EM field may take a non-zero value. This is the case of the linear momentum of the EM field when quantum fluctuations couple to a medium in which both parity (P) and time-reversal (T) symmetries are broken. In particular, the constitutive equations of a magneto-electric medium contain a non-reciprocal (nr) EM susceptibility [9], \(\chi_{\text{nr}}^{\text{EM}}\), which results from broken P and T. Generally, \(\chi_{\text{nr}}^{\text{EM}}\) is an antisymmetric T,P-odd tensor which generates an electric polarization in response to a magnetic field, \(\Delta P = \chi_{\text{nr}}^{\text{EM}} \cdot B\) and conversely, a magnetization as a response to an electric field, \(\Delta M = -\chi_{\text{nr}}^{\text{EM}} \cdot E\). As a result of the matter-field coupling and momentum conservation, linear momentum can be transferred from the EM vacuum to matter during the process that controls the breakdown of the symmetries. A nonzero tensor \(\chi_{\text{nr}}^{\text{EM}}\) is found in any medium in crossed external electric and magnetic fields, in a moving dielectric medium and in a chiral medium exposed to a magnetic field [10]. In this article we concentrate on the latter case.

It is a generic phenomenon in field theory that the breakdown of a symmetry is accompanied by a non-zero vacuum expectation value (VEV) of some physical observable associated with the symmetry. In our case the P and T symmetries happen to be broken explicitly by the presence of a chiral molecule and the action of an external magnetic field, \(B_0\). Correspondingly, a non-zero VEV of the EM momentum shows up in the direction along which the symmetries are
density

yield, broken, \(B_0\). The question arises whether it could be possible to take advantage of this phenomenon for practical purposes. To this end we will show that, due to the conservation of total linear momentum, there exists necessarily a transfer of kinetic momentum to the chiral molecule of equal magnitude and opposite sign to the VEV of the EM momentum.

Also, in the context of high energy physics, it is known that the electro-weak interaction violates the P and T symmetries [11, 12] and CP (i.e. T) is also expected to be naturally broken in QCD. In the latter case, the existence of a light pseudo-scalar particle, the axion, has been postulated as a solution of the so-called CP problem [13] and indirect observations of the axion through its coupling to the EM field have been suggested [14] and put into practice [15]. In the PVLAS experiment [15] signatures of the axion–photon interaction are investigated through the anomalous rotation of the polarization direction of optical light in the presence of an intense magnetic field, similar to the vacuum birefringence effect expected from the polarization of the QED vacuum [16, 17]. Nonetheless the rotation of the polarization axis of light may be caused by the breakdown of the P or T symmetries [16, 17].

In addition, the derivations of the above expressions for the conserved linear momentum are purely phenomenological and lack an explicit quantum interaction Hamiltonian between matter and radiation. Also, a macroscopic approach can easily lead to an erroneous prediction. For instance, it is shown in [10] that for a chiral distribution of electrically polarizable molecules in an external magnetic field, \(E(r) \wedge B^* (r) = 0\) should hold locally, although the medium contains a nonzero non-reciprocal effective (eff) response which would make \(\langle E_{\text{eff}} \wedge B_{\text{eff}} \rangle \neq 0\). Another problem that should be resolved in a quantum microscopic treatment is the UV divergence of the expression for the quantum EM momentum density obtained in a homogeneous medium [21]. This line of investigation was started by Kawka, van Tiggeelen and Rikken in [22, 25], where they computed the Casimir momentum of an atom in crossed external electric and magnetic fields. The divergences were found there to disappear by mass renormalization and the leading quantum contribution was found to be a factor \(\alpha^2\) smaller than the classical EM momentum.

In [1] we reported the quantum computation of the Casimir momentum for a chiral molecule in a uniform external magnetic field. In our model chirality breaks the parity symmetry and the magnetic field breaks time reversal, so it is symmetry allowed to have a non-vanishing value for the momentum of the electromagnetic field. In this case we performed a semiclassical computation of the Casimir momentum for the same model and compare it with the quantum result. We explain the physical mechanisms which mediate the transfer of linear momentum from the EM vacuum to the chiral molecule and we analyze the transfer of energy.

The article is organized as follows. In section 2 we present the model. Next, we perform a semiclassical computation of the total EM linear momentum.
the Casimir momentum in section 3. In section 4 we review the quantum computation of [1], paying special attention to the physical mechanisms involved in the transfer of momentum. In section 5 we explain the exchange of energy between molecule, quantum vacuum and magnetic field. In section 6 we summarize our conclusions.

2. The model

We propose the simplest model for a chiral molecule that exhibits all necessary features to leading order in perturbation theory: broken mirror symmetry, Zeeman splitting of energy levels and coupling to the quantum vacuum and we neglect relativistic effects. In our model the optical activity of the molecule is determined by a single chromophoric electron within a chiral object which is further simplified to be a two-particle system in which the chromophoric electron of charge $q_e = -e$ and mass $m_e$ is bound to a nucleus of effective charge $q_N = e$ and mass $m_N \gg m_e$. The binding interaction is modeled by a harmonic oscillator potential, $V^{HO} = \frac{1}{2} \omega^2 (x^2 + y^2 + z^2)$, to which we add a term $V_{C} = C x_{yz}$ to break the mirror symmetry perturbatively in first order. The coordinates $x$, $y$, $z$ are those of the relative position vector, $r = r_N - r_e$, and $\mu = \frac{m_N m_e}{m_N + m_e}$. The center of mass position vector is $R = (m_N r_N + m_e r_e)/M$ with $M = m_N + m_e$.

The conjugate momentum of $r$ is $p = \mu (p_N/m_N - p_e/m_e)$, while the conjugate momentum of $R$ is the total conjugate momentum, $P = p_r + p_x$. $V_C$ was first introduced by Condon et al. [26, 27] to explain the rotatory power of chiral compounds with a single oscillator model. Both the anisotropy in $V^{HO}$ and the chiral potential $V_C$ are determined by the Coulomb interaction of the two-body system with the rest of the atoms within the molecule. In particular, the parameter $C$ is the sum of all third order coefficients of the expansion of the Coulomb interaction of the chromophoric group with the surrounding charges around their mean distance [see equation (42) of [27]]. It is a pseudo-scalar which does not necessarily vanish for a chiral environment. In principle, all parameters of this model can be computed ab initio from the experimental data [27].

When an external uniform and constant magnetic field $B_0$ is applied the total Hamiltonian of the system reads,

$$H = H_0 + H_{EM} + W,$$

where

$$H_0 = \sum_{i=1}^{N} \frac{1}{2m_i} \left( p_i - q_i A_0(r_i) \right)^2 + V^{HO} + V_C,$$

(1)

and

$$H_{EM} = \sum_{k,e} \hbar \omega_k (a_{ke}^\dagger a_{ke} + \frac{1}{2}) + \frac{1}{2} \mu_0 \int d^3r B_0^2,$$

(2)

$$W = \sum_{i=1,e} \frac{-q_i}{m_i} \left( p_i - q_i A_0(r_i) \right) \cdot A(r_i) + \frac{q_i^2}{2m_i} A^2(r_i),$$

(3)

with $W$ is the minimal coupling interaction potential. In the vector potential we have separated the contribution of the external classical field, $A_0(r_i) = \frac{1}{2} B_0 \times r_i$, from that of the quantum field operator, $A(r_i)$. Note that, having incorporated the internal electrostatic interaction of the two-body system within $V^{HO}$ and the electrostatic interaction of the system with the surrounding within $V_C$, the EM vector potential in $W$ is just transverse. In the sum, $a_{ke}$ and $a_{ke}^\dagger$ are the creation and annihilation operators of photons with momentum $\hbar k$, frequency $\omega_k = \epsilon k$ and polarization vector $\epsilon$ respectively. The magneticostatic energy is a constant irrelevant to us that we will discard.

In the absence of coupling to the vacuum field, the system with Hamiltonian $H_0$ possesses a conserved pseudo-momentum, $K_0 = p_k + \epsilon B_0 \times r$, which satisfies $[H_0, K_0] = \theta$ and has continuous eigenvalues $Q$. Here $p_k$ is the kinetic momentum of the center of mass, $P_{EM} = \mu R$, which relates to $P$ through $P_{EM} = P - \frac{1}{2} B_0 \times r - e[A(r_N) - A(r_e)]$. The unitary operator $U = \exp [i (Q - \frac{1}{2} B_0 \times r) \cdot R/\hbar]$ maps the Hamiltonian $H_0$ into $\tilde{H}_0 = U^\dagger H_0 U$, which conveniently separates the motion of the center of mass from the relative motion [28, 29].

$$\tilde{H}_0 = \frac{1}{2M} Q^2 + \frac{1}{2\mu} p^2 + V^{HO} + V_C + V_Z + \Delta V.$$  (4)

In this equation $V_Z = \frac{C}{2\pi} (r \cdot p) \cdot B_0$ is the Zeeman potential with $\mu = \frac{m_N m_e}{m_N + m_e}$. Terms of order $QB_0$ and $B_2^2$ are cast in $\Delta V = (e^2/2)(1/M + \mu/\mu^2) (r \cdot B_0)^2 + eQ \cdot (r \times B_0)/M$. In the following, both $V_C$ and $V_Z$ will be considered first order perturbations to the harmonic oscillator potential and higher order perturbative terms like those in $AV$ will be neglected.

The ground state of the Hamiltonian $H_0$ is, up to order $CB_0$ in stationary perturbation theory, 

$$|\tilde{\Omega}_0 \rangle = |0\rangle - C |111\rangle - i \sum_{\eta \in \{\pm 1\}} \left( |100\rangle + 2 |221\rangle \right)$$

$$- \sqrt{2} i \sum_{\eta \in \{\pm 1\}} \left( |002\rangle + 2 |201\rangle \right)$$

$$+ \sum_{\text{cyclic permutations}}.$$  (5)

Correspondingly, the ground state of $H_0$ is $|\Omega_0 \rangle = U|\tilde{\Omega}_0 \rangle$, with a pseudo-momentum $Q_0$ to be fixed. The fact that $\langle \Omega_0 | r | \Omega_0 \rangle = 0$ implies that $Q_0$ is the kinetic momentum of the oscillator, i.e. no other contribution exists to the pseudo-momentum ($K_0$) of the bare molecule in its ground state. In the above equation the states $|n_1, n_2, n_3\rangle$ refer to the eigenstates of the harmonic oscillator Hamiltonian. The dimensionless parameters are: $B_0 = \frac{eB_0}{\hbar \sqrt{\mu m_0}}$ with $i \neq j \neq k$ and $i \neq k$, $C = \frac{\hbar \omega_k}{2(2\pi)^{1/2}}$, $\eta^{ij} = \frac{m_0 - m_j}{m_0 + m_i}$. Here, the indices $i, j, k$ take on the three spatial directions, $x, y, z$. The $\eta$ factors are assumed to be small quantities which quantify the anisotropy of the oscillator. They all have to be nonzero for the optical activity of the molecule to survive rotational averaging. The dimensionless parameters, $C, B_0$ and $\eta^{ij}$, are the expansion parameters of our perturbative calculations. We will restrict to the lowest order in them all.

3. Semiclassical approach

In [10] van Tiggelen has derived an expression for the Casimir momentum using a Green’s function formalism which is compatible with Nelson’s prescription. That formalism was later applied in [30] to compute the Casimir momentum in a configuration of magnetic dipoles disposed in a twisted H configuration.
In our case we are interested in the Casimir momentum in the presence of a single molecule. As noticed in [18], the Casimir momentum which derives from Abraham and Nelson’s prescriptions coincides approximately for a diluted medium (same applies to the forces generated by time varying fields). For the case of a single particle the so-called Abraham momentum reads \( d \land B \), \( d \) being the electric dipole moment of the molecule. Here we apply a linear response formalism upon \( d \land B \) following a similar semiclassical treatment to the one for the Lamb shift of a single dipole or the one for the van der Waals forces between atoms [32–34]. This is equivalent to the Green’s function formalism of [10, 30] considering a single magnetoeclaret.

We aim to compute the vacuum expectation value \( P^{\text{Cas}} = \Re\{ (d \land B) \} \). We start the calculation by decomposing both the electric dipole operator and the magnetic field into induced (\( \text{ind} \)) and free (\( \text{fr} \)) components. The induced operators relate to the free operators through the linear susceptibilities and Green’s functions. Any space-time dependent free operator \( X_{\text{fr}}(R; t) \) can be written in Fourier space as a sum of positive and negative frequency components, \( X_{\text{fr}}(R; \omega) = \int_0^\infty d\omega [X_{\text{fr}}(R; \omega) e^{-i\omega t} + X_0^\text{fr}(R; \omega) e^{i\omega t}] \), where \( X_0^\text{fr}(R; \omega) \) and \( X_{\text{fr}}(R; \omega) \) are the \( \omega \)-mode creation and annihilation operators of \( X_{\text{fr}} \) respectively. In the following we will be interested in the EM field and dipole moment operators evaluated at the position of the molecule, \( R_0 \). Therefore, unless necessary, we will omit the dependence of the operators on the position. In the case of the electric field of a plane wave propagating in free space in the direction \( \hat{k} \), we find \( E_{\text{fr}}(R; \omega) \propto e^{ik\cdot R} \), with \( k = \omega \hat{k}/c \) and likewise for the magnetic field. Therefore, together with the dependence on \( \omega \) we will add the dependence on \( k \) to the electric field annihilation/creation operator of a plane wave, \( E_{\text{fr}}(k, \omega) \) —idem for the magnetic field.

Since the relation between induced and free operators is linear and the action of annihilation operators on the vacuum vanishes, it follows from \( P^{\text{Cas}} = \Re\{ (d \land B) \} \) that

\[
P^{\text{Cas}} = \Re\{ (d_{\text{fr}} \land B_{\text{ind}}) \} + \Re\{ (d_{\text{ind}} \land B_{\text{fr}}) \}. \tag{6}
\]

In [35] we have obtained the constitutive equations of our magneto-chiral model by computing the response of the molecule to a monochromatic EM plane wave of frequency \( \omega \) and wave vector \( k \). Up to electric quadrupole contributions, the induced electric dipole moment operator reads,

\[
d_{\text{ind}}(\omega) = \alpha_E \delta_{ij} E_{\text{fr}}(k, \omega) + \chi \epsilon_{ijk} B_{\text{fr}}^i(k, \omega)
+ \beta \delta_{ij} B_{\text{fr}}^i(k, \omega) + \gamma \epsilon_{ijk} B_{\text{fr}}^i(k, \omega) + \frac{1}{2} \xi \left[(B_0 \cdot k) E_{\text{fr}}(k, \omega) + (B_0 \cdot E_{\text{fr}}(k, \omega))k_i\right],
\]

where a rotational average is implicit in this equation. The factor \( \alpha_E \) is the ordinary electric polarizability, \( \chi \) describes the Faraday effect, \( \beta \) is the molecular rotatory factor responsible for the natural optical activity and \( \gamma \) and \( \xi \) give rise to the magnetoeclaret anisotropy. The expressions of all these factors have been summarized in appendix A. It has been shown in [35] that, once the rotational power and the refractive index of a compound are given —i.e. the parameters \( \alpha_E \) and \( \beta \), all other parameters of our model can be deduced.

Defining the effective electric polarizability and the crossed magneto-electric polarizability tensors respectively as,

\[
\alpha_E^{ij}(k, \omega) = [\alpha_E + \frac{1}{2} \xi (B_0 \cdot k)] \delta^{ij} + k^i B_0^j - i\omega \epsilon_{ijk} B_0^k,
\]

\[
\alpha_E^{ij}(k, \omega) = i\omega \epsilon^{ijk} \chi \epsilon_{ijk} B_0^j, \tag{8}
\]

we can write equation (7) as,

\[
d_{\text{ind}}(\omega) = \alpha_E^{ij}(k, \omega) E_{\text{fr}}(k, \omega) + \alpha_E^{ij}(k, \omega) B_{\text{fr}}(k, \omega). \tag{9}
\]

Using Maxwell’s equation for the free fields, \( \dot{E}_{\text{fr}} = \nabla \land B_{\text{fr}} \), we can write \( d_{\text{ind}}(\omega) \) as a response to the free electric field alone,

\[
d_{\text{ind}}(\omega) = \alpha_E E_{\text{fr}}(k, \omega) + \chi \epsilon_{ijk} B_{\text{fr}}^i(k, \omega)
+ \beta \delta_{ij} E_{\text{fr}}(k, \omega) + \gamma \epsilon_{ijk} E_{\text{fr}}^i(k, \omega)
+ \frac{1}{2} \xi \left[(B_0 \cdot k) E_{\text{fr}}(k, \omega) + (B_0 \cdot E_{\text{fr}}(k, \omega))k_i\right]. \tag{10}
\]

From here it is obvious that the non-reciprocal response comes from the fourth term on the r.h.s., which depends on the relative direction of the wave vector, \( k \), with respect to the external magnetic field. We will denote this non-reciprocal (nr) polarizability by \( \alpha_{nr}(k, \omega) = (\xi/2 - \gamma/\omega)(B_0 \cdot k) \). It is at the origin of the magnetoeclaret birefringence [35]. The induced magnetic field can be written as a linear response to the free dipole located at \( R_0 \),

\[
B_{\text{ind}}(R, \omega) = \epsilon_0^{-1} \left[c^{-1} g_m^{(0)}(R, R_0; \omega) \cdot d_{\text{fr}}(R_0, \omega)
+ c^{-1} g_m^{(0)}(R, R_0; \omega) \cdot m_{\text{fr}}(R_0, \omega)ight], \tag{11}
\]

where \( m_{\text{fr}}(R_0, \omega) \) is the \( \omega \)-mode of the free magnetic dipole moment operator and the Green functions \( g_m^{(0)}(\cdot , \cdot ; \omega) \) relates to the Green function of Maxwell’s equation for the EM vector potential in free space,

\[
\left[\omega^2 \mathbf{\nabla} \land \mathbf{\nabla} - \xi \left\{ g_m^{(0)}(R - R', \omega) = \delta^{(3)}(R - R') \mathbf{\nabla} \land \mathbf{\nabla} \right\}
\right. \tag{12}
\]

through \( g_m^{(0)}(R, R'; \omega) = \mathbf{\nabla} \land \left. g_m^{(0)}(R, R'; \omega) \right. \land \mathbf{\nabla} \land \mathbf{\nabla} \) and \( g_m^{(0)}(R, R'; \omega) = ik \mathbf{\nabla} \land g_m^{(0)}(R, R'; \omega) \).

When substituting the induced operators in equation (6) as functions of the free operators we find the vacuum expectation values of bilinear operators. Those expectation values (dipole and field quadratic fluctuations) relate to the imaginary part of their respective linear response functions through the fluctuation-dissipation theorem [31],

\[
\langle B_{\text{fr}}(R, \omega) \otimes E_{\text{fr}}(R', \omega') \rangle
= \frac{\hbar}{\pi \epsilon_0 c} \Im\{ g_m^{(0)}(R, R'; \omega) \delta(\omega - \omega') \},
\]

\[
\langle B_{\text{fr}}(R, \omega) \otimes B_{\text{fr}}(R', \omega') \rangle
= \frac{\hbar}{\pi \epsilon_0 c^2} \Im\{ g_m^{(0)}(R, R'; \omega) \delta(\omega - \omega') \},
\]
of 'dressed' normal modes, we can write the above integral as the sum over the momenta $G$(\omega), hence, following Croze’s argument \[ 24\] upon the location of the only molecule at $R_0$. In the last equation above we use the result obtained in \[ 35\], $\alpha_{EM} = - \alpha_{ME}$ and we restrict to nonreciprocal terms for simplicity. Using the linear response relations of equations (9) and (11) in equation (6) and applying the expectation values of equation (13) we end up with the relation,

$$P_{\text{Cas}} = -\frac{\hbar^2}{1458\pi^2} eC B_0 \int_0^\infty d\omega \omega B_0 \Im \left\{ \frac{1}{\pi} \right\}$$

where $\omega_0 = (\omega_x + \omega_y + \omega_z)/3$. It is remarkable that the frequency integral does not present any UV divergence, unlike the expression for $P_{\text{Cas}}$ in \[ 21\] for a magneto-electric medium in crossed fields. We will see later on that this semiclassical result is included in the microscopic QED result, but it enters as a small correction to the leading term.

### 4. Quantum approach

The system of the Hamiltonian $H$ possesses a conserved pseudo-momentum \[ 25, 28, 29\],

$$K = P + \frac{e}{2} B_0 \wedge r + \sum_{k,\epsilon} \hbar k(\alpha_{\epsilon E}^k a_{-k} + \frac{1}{2})$$

which satisfies $[H, K] = 0$. Its eigenvalues are therefore good quantum numbers. The terms in $K$ can also be arranged as,

$$K = P_{\text{kin}} + P_{\text{Abr}} + P_{\text{Cas}} + P_{\text{Coul}}$$

where, beside the kinetic momentum, $P_{\text{Abr}} = eB_0 \wedge r$ is the Abraham momentum and we define the Casimir momentum operator, $P_{\text{Cas}} = P_{\text{Cas}}^\parallel + P_{\text{Cas}}^\perp$, as the momentum operator of the vacuum field. $P_{\text{Cas}}$ is composed of a longitudinal Casimir momentum, $P_{\text{Cas}} = e[A(r) - A(0)]$ and a transverse Casimir momentum, $P_{\text{Cas}}^\perp = \sum_{k,\epsilon} \hbar k(\alpha_{\epsilon E}^k a_{-k} + \frac{1}{2})$ \[ 36\]. The latter is just the sum of the momenta $\hbar k$ of radiative photons. The longitudinal momentum is more subtle. It stems from the transverse electromagnetic gauge field coupled to electric charges. Note that in the Coulomb gauge $A$ is fully transverse. $P_{\text{Cas}}$ is referred to as a ‘longitudinal’ component since it can be written as the integral over the vector product of the longitudinal Coulomb electric field and the magnetic field generated by the charges, $e_0 \int d^3r E_{\text{Coul}} \wedge B$ \[ 36\].

Under the action of a time-varying magnetic field, $B_0(t)$, the time derivative of the expectation value of $K$ in the ground state, $\langle K \rangle$, vanishes,

$$\frac{d\langle K \rangle}{dt} = i\hbar^{-1} [H, K] + e \frac{\delta B_0(t)}{\delta t} \wedge \langle r \rangle = 0$$

This follows from $[H, K] = 0$ and $\langle r \rangle = 0$ for the chiral but unpolarized ground state\[ 5\]. The latter ensures also that the variation of the Abraham momentum vanishes in the ground state. From the expectation value of equation (20) it follows that, for an arbitrary variation of the magnetic field, the variation of the kinetic momentum of the chiral oscillator is equivalent in magnitude and opposite in sign to the variation of the Casimir momentum of the vacuum field,

$$\delta \langle P_{\text{kin}} \rangle = - \delta \langle P_{\text{Cas}} \rangle$$

$^5$ The oscillator in motion generates a dipole moment $\alpha_E(0) Q_0 \wedge B_0/M$ \[ 28, 29\].
Let us consider the molecule initially at rest in its ground state at zero magnetic field. During the switching of the magnetic field equation (21) implies that \( \langle P_{\text{las}} \rangle = -\langle P_{\text{Cas}} \rangle \) at any time. This relation makes the Casimir momentum an observable quantity. In particular this equality holds well after the switching has ended and the magnetic field achieves a stationary value \( B_0 \). In the following we evaluate the Casimir momentum in the asymptotically stationary situation in which the molecule is in its ground state at constant kinetic momentum, \( Q_0 \), constant magnetic field, \( B_0 \) and once coupled to the EM vacuum. We denote by \( \Omega \) this asymptotic state of the molecule, which we will compute applying up to second order perturbation theory to \( \langle \Omega_0 \rangle \) with the interaction potential \( W \). We define \( \langle P_{\text{Cas}} \rangle = \langle \Omega | P_{\text{Cas}} | \Omega \rangle \) and calculate separately the transverse momentum, \( \langle P_{\perp} \rangle = \sum_{k,e} h^2 k \langle \Omega | a^e_k a_k^e | \Omega \rangle \) and the longitudinal momentum, \( \langle P_{\parallel} \rangle = e \langle \Omega | A(r_e) - A(r_0) \rangle \Omega \).

### 4.1. Transverse Casimir momentum

For the computation of \( \langle P_{\perp} \rangle \) at \( O(\langle B_0 \rangle) \) and lowest order in the fine structure constant, \( \alpha = e^2 / 4\pi\epsilon_0\hbar c \), we need to compute \( |\Omega_0 \rangle \) applying second order perturbation theory to \( |\Omega_0 \rangle \). Note that this implies applying up to fourth-order perturbation theory in \( V_2 + V_c + W \) to the ground state of the harmonic oscillator Hamiltonian. \( |0 \rangle \). We use the U-transformed states and the U-transformed potential, with \( U = \exp [ -i \gamma_{0}^e (B_0 \wedge \cdot \cdot \cdot R) ] \),

\[
\begin{align*}
\tilde{W} &= -\frac{e}{m_N} \left( \frac{p + m_N}{M} P - \frac{e}{2} B_0 \wedge \cdot R \right) \cdot A \left( \frac{R + m_e}{M} \right) \\
&= \frac{e^2}{2m_N} (R + m_e) \cdot A \left( \frac{R + m_N}{M} \right) + \frac{e^2}{2m_e} A^2 \left( \frac{R - m_N}{M} \right),
\end{align*}
\]

(22)

to arrive at,

\[
\langle P_{\perp} \rangle = \sum_{Q_0, \Omega_0} \sum_{Q, I, \gamma} \sum_{\gamma_{0}^e, k, e} h^2 Q_0^2 / 2M + E_0 - E_{Q,l,k} \times \langle Q, I, \gamma | h\gamma_{0}^e a^e_{-1} a_k^e | \rangle \langle Q | I \rangle \otimes | \gamma_{0}^e \rangle \times h^2 Q_0^2 / 2M + E_0 - E_{Q,l,k} \}
\]

(23)

where \( |Q_0, \Omega_0 \rangle = \exp (iQ_0 \cdot R / \hbar \Omega_0) \), \( E_0 = \hbar (\omega_e + \omega_e + \omega_e) / 2 = \hbar \omega_0 / 2 \) and \( E_{Q,l,k} = E_{Q,l,k} \) are the energies of the intermediate states, \( (Q, I, \gamma) = (Q, I) \otimes | \gamma_{0}^e \rangle \) (idem for the prime states). The atomic states \( (Q, I) \) are eigenstates of \( H_0 \) and may have a priori any pseudo-momentum \( Q \). The EM states, \( | \gamma_{0}^e \rangle \), are 1-photon states with momentum \( \hbar \gamma_{0}^e \) and polarization vector \( e \). Zeros in the denominator are avoided in the summation. Writing the EM quantum field in equation (22) as usual [37],

\[
A(r) = \sum_{k,e} \sqrt{\frac{\hbar}{2\epsilon k \gamma_{0}^e}} [e a_k e^{ikr} + e^* a^e_k e^{-ikr}],
\]

(24)

with \( V \) a generic volume; passing the sums over \( Q, Q', k, k' \) and \( k'' \) in equation (23) to continuum integrals and by summing over polarization states we arrive at,

\[
\langle P_{\perp} \rangle = \frac{\hbar^2 e^2}{2\epsilon m_e} \int \frac{d^3k}{(2\pi)^3} \times \langle \Omega_0 | \left( p/2m_e - Q_0 - \frac{e}{2} B_0 \wedge \cdot R \right) e^{-i\frac{e}{\hbar}k \cdot r} + \left( p/m_N + Q_0 - \frac{e}{2} B_0 \wedge \cdot R \right) e^{i\frac{e}{\hbar}k \cdot r} \right] \times \langle \Omega | \left[ \left( h^2 k^2 / 2M + \hbar c k \cdot - \hbar c Q_0 / M - E_0 + H_0 \right)^2 \times e^{-i\frac{e}{\hbar}k \cdot r} \left( p/m_N + Q_0 - \frac{e}{2} B_0 \wedge \cdot R \right) \right] \Omega_0 \rangle.
\]

In this equation we can distinguish four terms. In two of them the exponentials to the r.h.s. and l.h.s. of the fraction compensate. They correspond to the Feynman diagrams in which a photon is created and annihilated at the position of one of the particles, i.e. either at the nucleus or at the electron position (figure 1(a)) and figure 1(b), respectively. In the other two terms the exponentials amount to \( \exp \pm i k \cdot r \). They correspond to the Feynman diagrams in which the virtual photons are created and annihilated in different particles (figure 1(a)) and figure 1(b)). In the latter the complex exponentials evaluated in the states of the harmonic oscillator yield an effective cut-off for the momentum integrals at \( k_{\max} \sim \sqrt{\mu_0 / \hbar} \), making their contribution negligible w.r.t. the other diagrams. Among the diagrams of figure 1(a) the dominant one is (b) in which virtual photons are created and annihilated at the electron position, as for the non-relativistic calculation of the Lamb shift [4]. It reads,

\[
\langle P_{\perp} \rangle = \frac{\hbar^2 e^2}{2\epsilon m_e} \int \frac{d^3k}{(2\pi)^3} \times \langle \Omega_0 | \left( m_N Q_0 + p + \frac{e}{2} B_0 \wedge \cdot R \right) e^{-i\frac{e}{\hbar}k \cdot r} \times \langle \Omega | \left[ \left( h^2 k^2 / 2M + \hbar c k \cdot - \hbar c Q_0 / M - E_0 + H_0 \right)^2 \times e^{i\frac{e}{\hbar}k \cdot r} \left( p/m_N + Q_0 - \frac{e}{2} B_0 \wedge \cdot R \right) \right] \Omega_0 \rangle.
\]

(25)

For the above integral not to vanish, the product of the quantum operators in the integrand must be even in \( k \). We observe that when moving the complex exponential on the l.h.s. to the r.h.s. of the fraction, respecting the canonical commutation relations the momentum \( p \) in \( H_0 \) gets shifted, \( p \rightarrow p - \frac{me}{\hbar} \hbar c k \cdot \),

\[
e^{-i\frac{e}{\hbar}k \cdot r} \left( h^2 k^2 / 2M + \hbar c k \cdot - \hbar c Q_0 / M - E_0 + H_0 \right)^{-1} \times e^{i\frac{e}{\hbar}k \cdot r} = \left[ h^2 k^2 / 2M + \hbar c k \cdot - \hbar c Q_0 / M - E_0 + H_0 \right]^{-1} \times e^{-i\frac{e}{\hbar}k \cdot r} \left( p/m_N + Q_0 - \frac{e}{2} B_0 \wedge \cdot R \right) \Omega_0 \rangle.
\]

As a result, the recoil kinetic energy in the denominators of equation (25) becomes \( h^2 k^2 / 2m_e \) and an additional term \( -\hbar c k \cdot p/m_e \) shows up there. Because the internal velocity of the electron is generally much greater than the center of mass velocity, \( p/m_e \gg Q_0 / M \), the term \( \hbar c k \cdot Q_0 / M \) will be a
Virtual photons of momentum \( k \) for the case of \( \langle \omega \rangle \) contributing to \( \langle I \rangle \) evaluated between the ground state and an intermediate state, say our non-relativistic approach [38]. This yields an even factor \( \frac{\hbar}{m_e c^2} \) is the non-relativistic Doppler shift, which does not clash with the 

\[
\delta M \approx \frac{\hbar k}{2m_e c^2} + \hbar k c - E_0 + H_0 \quad (k \cdot p) \\
\times \frac{1}{\left( \frac{\hbar^2 k^2}{2m_e c^2} + \hbar k c - E_0 + H_0 \right)^2} (p + \frac{\hbar}{2}B_0 \wedge r) \langle \Omega_0 \rangle.
\]

At the same time, since both the chiral interaction \( V_C \) and the Zeeman potential \( V_Z \) featuring in \( H_0 \) are treated as perturbations to the harmonic oscillator, the denominator is to be expanded up to order \( \mathcal{O}(V_C) \) and only terms at \( \mathcal{O}(CB_0) \) must be retained. The calculation includes a number of finite integrals of the form,

\[
\Re \int_0^\infty k^3 \, dk \frac{1}{(E_k - E^\text{vac})(E_k - E^\text{vac})^2} \\
+ \frac{1}{(E_k^\text{vac} - E_2)(E_k^\text{vac} - E_1)^2} \\
\approx \frac{2m_e^2}{\hbar^2 (E_1 - E_2)^2} \left[ \log \left( \frac{E_1}{E_2} \right) + \mathcal{O}(\hbar c/m_e c^2) \right] \\
+ \mathcal{O}(\hbar c/m_e c^2)^2 + \ldots
\]

where \( E_k^\text{vac} = \hbar k^2/2m_e + \hbar k c \) and \( E_1,2 \) are the energies of the electronic transitions between intermediate states, which are of the order of \( \hbar \omega_0 \).

Additional integrals involving the product of three and four fractions appear also in equation (26) which yield terms of the same orders. The final expression can be greatly simplified assuming small anisotropy factors, \( \eta_{ij} \ll 1 \). Averaging over the molecule’s orientations (rot) [33] and expanding the result up to leading order in the anisotropy factors we obtain,

\[
\langle P_{\perp}^{\text{Cas}} \rangle_{\text{rot}} = [20736 \ln (4/3) - 12928 \ln (2) - 14511] \\
\times \frac{Ce^3 B_0}{93312 \pi^2 c e \omega_0^3 \omega_0 \omega_c \omega_e} \eta^{\text{zz}} \eta^{\text{zx}} \\
\approx \frac{-1.06 Ce^3 B_0}{144 \pi^2 c e \omega_0^3 \omega_0 \omega_c \omega_e} \eta^{\text{zz}} \eta^{\text{zx}} \eta^{\text{zx}}.
\]

It is clear that \( \langle P_{\perp}^{\text{Cas}} \rangle_{\text{rot}} \) is the expression to be compared with the semiclassical result of equation (18), since from equation (17) we read that the semiclassical \( P_{\perp}^{\text{Cas}} \) is the momentum of the radiative (i.e. transverse) modes only. First we observe that \( \langle P_{\perp}^{\text{Cas}} \rangle_{\text{rot}} \) is a factor \( (m_ec^2/\hbar \omega_0)^2 \) times larger than the semiclassical \( P_{\perp}^{\text{Cas}} \). From equation (27) we have that the semiclassical result is included in our quantum calculation (there are no other terms of the same order in the diagrams neglected), but it enters at a second order correction, \( \mathcal{O}(m_ec^2/\hbar \omega_0)^2 \), to the leading term. We conclude that the reason for this discrepancy is the failure of the semiclassical approach to account for the Doppler effect due to the relative motion of the internal charges in order to generate the necessary spectral non-reciprocity. Instead, spectral non-reciprocity comes in the semiclassical approach from the effective magneto-chiral birefringence. We also note that the result of equation (28) assumes an integration over \( k \) up to

\[\Delta k \sim \sqrt{\hbar/\mu \omega_0}.\]
infinity in equation (26), which violates the non-relativistic limit. However, had we assumed a cut-off for \( k_{\text{max}} \) of the order of the inverse of the Compton electronic wavelength, \( k_{\text{max}} \sim m_e c / h \), the expression on the r.h.s. of equation (28) would change by only a factor of order unity.

### 4.2. Longitudinal Casimir momentum

For the computation of \( \langle P_{\text{Cas}}^\parallel \rangle \) the details of the calculation have already been published in [1] and the supplemental material there. Here we concentrate on the underlying mechanism which originates the transfer of momentum from the vacuum field to the molecule. The calculation at \( O(CB_0) \) implies up to third-order perturbation theory in \( V_Z + V_C + W \) to the ground state of the harmonic oscillator Hamiltonian, [0],

\[
\langle P_{\text{Cas}}^\parallel \rangle = \sum_{Q,I,J_{\text{rot}}} \frac{(Q_0, \tilde{\Omega}_0) e \Delta A(Q, I, \gamma)(Q, I, \gamma) W(Q_0, \tilde{\Omega}_0)}{Q_0^2/2M + E_0 - E_{Q,I,k}} + \text{c.c.,}
\]

where \( (Q_0, \tilde{\Omega}_0) = \exp(iQ_0 \cdot R / h)(\tilde{\Omega}_0) \) and \( \Delta A = A(r_N) - A(r) \). The \( Q_0 \) dependent terms are shown in [1] to give rise to mass renormalization factors. As for the rest we have,

\[
\langle P_{\text{Cas}}^\parallel \rangle = \left[ -\frac{h e}{2 c_\infty} \int \frac{d^3 k}{(2 \pi)^3} \frac{Q_0}{h^2 k^2 / 2 m_e + h \epsilon + E_0 - \hat{E}_0} \times \exp \left[ \mu_0 e (Q_0, \tilde{\Omega}_0) + \text{c.c.,} \cdot \right] - \frac{m_e \rightarrow m_N} \right]
\]

(29)

where \( \frac{m_e \rightarrow m_N} \) means that the same expression within the square brackets must be evaluated exchanging \( m_e \) with \( m_N \) and subtracted. In contrast to \( \langle P_{\text{Cas}}^\perp \rangle \), no Doppler shift term enters the calculation and no spectral non-reciprocity exists.

Nonetheless the longitudinal momentum is also generated by the non-vanishing transient currents parallel to the external magnetic field. In this case, however, the currents are due to the internal motion of both the chromophoric electron and the nucleus, \( J_{e,N} = e \mu_0 e / m_e \). They are the sources of the magnetic fields at some point \( X \) measured w.r.t. the center of mass,

\[
B_{e,N}(X) = -\frac{\mu_0}{4 \pi} \cdot \frac{\hat{J}_{e,N} \wedge \hat{X}}{X^2} = -\frac{i \mu_0 e}{m_e} \int \frac{d^3 k}{(2 \pi)^3} e^{i k \cdot X} \frac{k \wedge p}{k^2}.
\]

(30)

Each of these magnetic fields, combined with the Coulomb field \( (Coul) \) of the respective charges, \( +e \) for the nucleus and \( -e \) for the electron,

\[
E_{e,N}(X) = \frac{\pm e}{4 \pi \epsilon_0} \frac{X}{X^2} = \mp \frac{e}{\epsilon_0} \int \frac{d^3 k}{(2 \pi)^3} e^{i k \cdot X} \frac{k}{k^2}.
\]

(31)

give rise to the longitudinal Casimir momentum of equation (29),

\[
\langle P^\parallel_{\text{Cas}} \rangle = \epsilon_0 \int d^3 X (E_{e}^{\text{Coul}}(X) \wedge B_e^\perp(X))
+ \epsilon_0 \int d^3 X (E_{e,N}^{\text{Coul}}(X) \wedge B_{e,N}^\perp(X)).
\]

(32)

In order to obtain an equivalence between equations (29) and (32), one of the \( k \) factors in the Fourier transform of the magnetic fields in equation (30) must be substituted by \( k + h \epsilon / 2c e, N - (E_0 - \hat{E}_0) / h c \), where the momentum shift comes from the sum over the intermediate states which enter the transient currents. It is clear that the only difference between the two terms of equations (29 and 32) is in the sign of the charges which enter the electrostatic fields and the masses which determine their respective currents. As a result, the addition of both terms must be proportional to \( f(m_e) - f(m_N) \), with \( f \) a real functional of the masses. The result is,

\[
\langle P^\parallel_{\text{Cas}} \rangle = \frac{C e^3}{96 \pi^2 c e_0 \mu^* (\omega_x + \omega_y + \omega_z)} \sum_{i,j,k} \epsilon_{ijk} B_{0}^{\parallel i j k} \frac{h \epsilon}{\kappa \omega_k}.
\]

(33)

where \( \epsilon_{ijk} \) is the three-dimensional Levi-Civita tensor, the indices \( i, j, k \) take on the axis labels \( x, y, z \) and \( i \) is a unitary vector along the \( i \) axis. After averaging over the molecule orientations we end up with,

\[
\langle P^\parallel_{\text{Cas}} \rangle_{\text{rot}} = \frac{C e^3 \ln m_N / m_e B_0}{144 \pi^2 c e_0 \mu^* (\omega_x \omega_y \omega_z)} \eta^{x y} \eta^{x z} \eta^{x x}.
\]

(34)

As for the transverse Casimir momentum, the above calculation holds if we take the upper limit of integration of equation (29) at infinity. Again, for a cut-off of the order of \( k_{\text{max}} \sim m_e c / h \), additional terms of the same order as those in equation (33) would have been obtained.

### 4.3. Casimir momentum as a function of optical parameters

Finally, adding up the transverse and the longitudinal contributions we obtain,

\[
\langle P^\parallel_{\text{Cas}} \rangle_{\text{rot}} = \frac{C e^3 B_0 [\ln (m_e / m_N) + 1]}{144 \pi^2 c e_0 \mu^* (\omega_x \omega_y \omega_z)} \eta^{x y} \eta^{x z} \eta^{x x}.
\]

(35)

This formula is a simple expression for \( \langle P^\parallel_{\text{Cas}} \rangle_{\text{rot}} \) in terms of the chiral parameter \( C \), the magnetic field and the natural frequencies of the oscillator. We can write it also in terms of the fine structure constant, \( \alpha \), the static optical rotatory power, \( \beta(0) \) and the static electric polarizability of the molecule, \( \alpha_E(0) \). By comparing the above expression with the formulas for \( \beta \) and \( \alpha_E \) in appendix A we obtain 7,

\[
\langle P^\parallel_{\text{Cas}} \rangle_{\text{rot}} \simeq \frac{2 \alpha}{9 \pi} \frac{\beta(0)}{\alpha_E(0)} [\ln (m_N / m_e) + 1] e B_0.
\]

(36)

In [1] we speculate that, apart from constants of order unity, this expression is model-independent. For a given set of natural frequencies, all the atomic lengths in the problem are determined by quantum mechanics. In particular, \( \beta(0) / \alpha_E(0) \) is a length, a fraction of the electronic Compton wavelength, that we identify with a chiral length, \( l_{ch} \). Therefore, we can write \( P^\parallel_{\text{Cas}} \sim \alpha e B_0 l_{ch} \) and thus interpret it as the leading QED correction to the classical Abraham momentum.

7 We have fixed here an erroneous minus sign appearing in [1].
5. Origin of Casimir-induced kinetic energy

In the preceding sections we have found that the chiral molecule acquires a kinetic momentum during the switching of the external magnetic field as a result of its interaction with the vacuum field. On the other hand we have shown that, as a result of the conservation of the total momentum \( \mathbf{K} \), there exists a transfer of linear momentum from the vacuum field to the molecule. The question arises whether the resultant variation of kinetic energy is provided by the vacuum field or by an external source. In the following we prove that this variation of kinetic energy is part of the energy provided or removed by the source of the external magnetic field to generate a vacuum correction to the molecular magnetization. That magnetization energy can be considered as part of the ‘magnetic Lamb energy’.

To this aim we make use of the Hellmann-Feynman-Pauli theorem [39]. According to this theorem, the variation of the total energy of a system in its ground state with respect to an adiabatic parameter, \( \lambda \), can be computed from the expectation value of the functional derivative of the Hamiltonian w.r.t. that parameter. The variation of the total energy is the work done over the system of interest by an external source responsible for the adiabatic variation of the parameter. If the parameter enters an interaction potential, \( W_{\text{int}} \), that work reads

\[
W_{\lambda} = \int_0^\lambda \delta \lambda' \langle \delta W_{\text{int}} / \delta \lambda' \rangle.
\]

For instance, this approach is used to compute intermolecular forces by considering their center of mass position vectors as adiabatic parameters [40].

In our case, the adiabatic parameter to be varied is the magnetic field, \( B_0 \) and the variation of energy to be computed is a magnetic energy, \( W_{B_0} \). Since \( B_0 \) enters \( V_C \) and \( W \) linearly and \( \Delta V \) quadratically in equation (4)\(^8\), the variation of the total energy of the system molecule–EM during the adiabatic switching of the magnetic field from 0 up to its final value \( B_0 \) is,

\[
W_{B_0} = \int_0^{B_0} \delta \mathcal{B}_0 \langle \delta (\bar{W} + V_Z + \Delta V) / \delta \mathcal{B}_0 \rangle
\]

\[
= \int_0^{B_0} \delta \mathcal{B}_0 \langle [\bar{W}_{2\mathcal{B}_0} + V_Z + \mathcal{B}_0 + 2 \langle \Delta V \rangle] / \mathcal{B}_0 \rangle,
\]

where in the last equality \( \bar{W}_{2\mathcal{B}_0} = (e^2/2)(r \wedge \mathcal{B}_0) \cdot [A(R - \frac{m_e}{e} r)/m_e - A(R + \frac{m_e}{e} r)/m_e] \) includes only the \( \mathcal{B}_0 \)-dependent terms of \( \bar{W} \). We note that \( \mathcal{B}_0 \) is the work done by the external source that generates the uniform magnetic field \( B_0 \) in the space occupied by the chiral molecule in the presence of the quantum vacuum. The expression within the square brackets in equation (38) is indeed the total magnetization of the molecule in its ground state, \( \langle M_{B_0} \rangle \), with a minus sign in front. Hence we can write,

\[
W_{B_0} = - \int_0^{B_0} \langle M_{B_0} \rangle \cdot \delta \mathcal{B}_0.
\]

Up to our level of approximation \( W_{B_0} \) must include terms of up to order two in \( C, B_0 \) and \( \alpha \). It follows that perturbation theory has to be applied up to order six in \( V_C + V_Z + \Delta V + \bar{W} \).

We first observe that at leading order in \( \Delta V \) and quadratic in \( V_Z \) and at zero order in \( V_C \) and \( \bar{W} \), \( W_{B_0} \) reduces to the magnetization energy of the diamagnetic molecule in the absence of a vacuum field, \( \sim - \sigma_M(0) B_0^2 \), \( \sigma_M(0) \) being the static magnetic polarizability given in appendix A. At higher order in perturbation theory, including the chiral potential and the vacuum field, we find a number of additional terms in \( W_{B_0} \). Most of these terms amount to variations in the energy of internal atomic levels, which are not relevant to us. We are however interested in those terms of \( W_{B_0} \), which are of the order of the variation of the kinetic energy of the chiral group, \( \Delta E_{\text{kin}}(B_0) = \langle Q_0 - \langle P^{\text{Cas}}(B_0) \rangle \rangle^2 / 2M - Q_0^2 / 2M \), for an initial kinetic momentum \( Q_0 \) at zero magnetic field. In the following we search for these terms by inspection and show that altogether they add up to give \( \Delta E_{\text{kin}} \). As a result, we can say that the variation of the kinetic energy is supplied by the source of the external magnetic field to produce a vacuum correction in the magnetization of the chiral molecule.

First we note that keeping finite the momentum of the molecule, \( \mathcal{Q}_0 \) and bearing in mind that during the adiabatic switching of the magnetic field \( \mathcal{Q}_0 \) equals \( Q_0 - \langle P^{\text{Cas}}(B_0) \rangle \), \( W_{B_0} \) contains terms quadratic in \( C, B_0 \) and \( \alpha \) from the application of perturbation theory to \( e^{-i\mathcal{Q}_0 \cdot \mathcal{R}/\hbar} \langle 0 \rangle \) up to order one in \( V_C \) and \( V_Z \) and up to order two in \( \bar{W} \), as for the computation of the Casimir momentum. Following the same steps as for the calculation of \( \langle P^{\text{Cas}} \rangle \), we start with the dressed ground state, \( | \mathcal{Q}_0, \mathcal{Q}_0 \rangle = e^{-i\mathcal{Q}_0 \cdot \mathcal{R}/\hbar} | \mathcal{Q}_0 \rangle \) and apply it to second order perturbation theory with the interaction potential \( \bar{W} \). The calculation is therefore similar to that of the ordinary Lamb shift except for the fact that the ground state and the intermediate states in our case are dressed up to first order in \( C \) and \( \mathcal{Q}_0 \). In addition to the diagram of figure 1i(b) for the self-energy of the electron we must add the one of figure 1i(a) for the nucleus. We will denote the resultant energy by \( E_{\text{Lamb}}(\mathcal{B}_0) \) and refer to it as magnetic Lamb energy,

\[
E_{\text{Lamb}}(\mathcal{B}_0) = \sum_{Q, I, Q_I, \gamma} \langle \mathcal{Q}_0, \mathcal{Q}_0 | \bar{W} | Q, I, I', \gamma | \mathcal{Q}_0, \mathcal{Q}_0 \rangle / \Omega_0 (2M + E_0 - E_{Q, I, k}).
\]

Let us reorganize first the terms in \( \bar{W} \) as

\[
\bar{W} = - \frac{e}{m_e} \left( p - \frac{e}{2} \mathcal{B}_0 \wedge r \right) \cdot A(r_N) + \frac{e}{m_e} \left( p + \frac{e}{2} \mathcal{B}_0 \wedge r \right) \cdot A(r_e) - \frac{P \cdot P^{\text{Cas}}}{M} + O(A^3).
\]

This shows that the longitudinal Casimir momentum appears naturally coupled to the canonical momentum of the center of mass. In the following we disregard the terms of \( E_{\text{Lamb}} \) associated with internal energies and restrict ourselves to those of the order of \( E_{\text{kin}} \). In the first place, from the combination of the factors \( -p \cdot \frac{e}{m_e} A(r_N) + \frac{e}{m_e} A(r_e) \) and \( -M^{-1} P \cdot P^{\text{Cas}} \) in \( \bar{W} \) we have,

\[
E_{\text{Lamb}}(\mathcal{B}_0) = \sum_{Q, I, Q_I, \gamma} \langle \mathcal{Q}_0, \mathcal{Q}_0 | e P \cdot A(r_e) / m_e | Q, I, I', \gamma | \mathcal{Q}_0, \mathcal{Q}_0 \rangle / \Omega_0 (2M + E_0 - E_{Q, I, k})
\]

\[
\times \langle Q, I, I' | Q_I | \gamma | e A(r_e) / P / M | \mathcal{Q}_0, \mathcal{Q}_0 \rangle + c.c.
\]

\[
- [m_e \rightarrow m_N].
\]
Since the ground state $|Q_0, \bar{\Omega}_0\rangle$ is an eigenstate of the center of mass canonical momentum, $P(Q_0, \bar{\Omega}_0) = Q_0 |Q_0, \bar{\Omega}_0\rangle$, the above equation can be written as

$$E_{1}^{\text{Lamb}} = \int \left( \sum_{Q, l, \gamma} |Q_0, \bar{\Omega}_0\rangle \langle p \cdot A(r_\gamma)/m_e|Q, l, \gamma\rangle \right) \frac{\Omega_0}{2M + E_0 - E_{Q, l, \gamma}} \times (Q, l, \gamma) \cdot \bar{\Omega}_0/2 + M + c.c. \right] \langle Q_0, \bar{\Omega}_0\rangle - [m_e \rightarrow m_N].$$

The expression under the sum is exactly the one for the longitudinal Casimir momentum in equation (29) with a minus sign in front. Therefore we find,

$$E_{1}^{\text{Lamb}} = -\langle P_{1}^{\text{Cas}}(\bar{\Omega}_0) \rangle \cdot \Omega_0/M.$$  \hspace{1cm} (43)

This relation explains the subscript $\parallel$ in $E_{1}^{\text{Lamb}}$.

Likewise, from the combination of two factors

$$-\frac{e^2}{N} (p + \frac{e}{2} \bar{B}_0 \wedge \bar{r}) \cdot A(r_\gamma) \text{ in } \mathbb{R}^2,$$

we have:

$$\sum_{Q, l, \gamma} |Q_0, \bar{\Omega}_0\rangle \langle p + \frac{e}{2} \bar{B}_0 \wedge \bar{r} \rangle \cdot A(r_\gamma) \langle Q, l, \gamma\rangle \cdot \bar{\Omega}_0/2M + E_0 - E_{Q, l, \gamma} \times (Q, l, \gamma) \cdot \bar{\Omega}_0/2 + M + E_0 + H_0 \times (p + \frac{e}{2} \bar{B}_0 \wedge \bar{r}) \langle \bar{\Omega}_0 \rangle.$$  \hspace{1cm} (44)

Next we note in the denominator a Doppler shift term due to the motion of the center of mass, $-h k \cdot Q_0/\Omega_0$. Expanding the fraction up to first order in this term and discarding the zero-order terms we find,

$$E_{1}^{\text{Lamb}} = \frac{-e^2}{2cm_e^2e_0} \int \frac{d^3k}{(2\pi)^3} \frac{h}{M} \langle k \cdot \bar{\Omega}_0 \rangle \left( p + \frac{e}{2} \bar{B}_0 \wedge \bar{r} \right) \times (1 - \frac{k^2}{p^2}),$$

$$\times \left( h^2 \delta_{2M} + h c k - h k \cdot p/m_e - h k \cdot \Omega_0/M - E_0 + H_0 \right)^2 \times (p + \frac{e}{2} \bar{B}_0 \wedge \bar{r}) \langle \bar{\Omega}_0 \rangle.$$  \hspace{1cm} (45)

Lastly, by expanding the denominator up to first order in $-h k \cdot p/m_e$ and comparing with equation (26) we end up with

$$E_{1}^{\text{Lamb}} = -\langle P_{1}^{\text{Cas}}(\bar{\Omega}_0) \rangle \cdot \Omega_0/M.$$  \hspace{1cm} (46)

We have found in section 4 that $(P_{1}^{\text{Cas}}(\bar{\Omega}_0) \propto \bar{B}_0$ in stationary conditions. Therefore, combining the results of equations (43) and (46) and considering equation (38) we can write the magnetic Lamb energy associated with these two terms as,

$$\int_{0}^{B_0} \delta_{\bar{B}_0} (E_{1}^{\text{Lamb}} + E_{1}^{\text{Lamb}}) /\bar{B}_0$$

$$\times (P_{1}^{\text{Cas}}(B_0))^2 /2M - Q_0 \cdot (P_{1}^{\text{Cas}}(B_0))/M,$$  \hspace{1cm} (47)

which equals $\Delta E_{\text{lin}}(B_0) = \langle Q_0 \cdot (P_{1}^{\text{Cas}}(B_0))^2 /2M - Q_0^2 /2M \rangle$ as anticipated. From this result we see that the variation of the kinetic energy of the chiral group, induced by the transfer of linear momentum from the vacuum to the molecule, has its origin in the magnetic Lamb energy (i.e. that part of the interaction energy that is induced by both the magnetic field and the quantum vacuum)\(^{9}\). This kinetic energy is the magnetic energy associated with the vacuum correction to the magnetization of the molecule, $\Delta M_{\text{e}} = -\langle E_{1}^{\text{Lamb}} + E_{1}^{\text{Lamb}}\rangle /\bar{B}_0$. The sign of this energy depends on the magnitudes of the initial momentum and final magnetic field, $Q_0$ and $B_0$, as well as on their relative orientation. A positive sign means that the energy is provided by the external source which generates the magnetic field. A negative sign means that part of the initial kinetic energy of the molecule is removed by the external source during the magnetization process.

6. Conclusions

We have derived an expression for the Casimir momentum transferred from the EM vacuum to a chiral molecule during the switching of an external magnetic field. We have modeled the chiral molecule using the single quantum oscillator model of Condon et al\(^{26, 27, 35}\). We have applied both a semiclassical approach and a fully quantum non-relativistic approach. The quantum approach reveals that two distinct mechanisms operate in the transfer of momentum, both based on the production of transient internal currents in the direction parallel to the external magnetic field. The transverse Casimir momentum (equation (26)) has its origin in the spectral non-reciprocity generated by a Doppler shift in the frequency of the vacuum photons. This shift is due to the internal momentum of the chromophoric electron, $p$. The breakdown of time reversal and mirror symmetry makes $p$ take a non-vanishing transient value parallel to the external magnetic field. On the contrary, the longitudinal Casimir momentum (equation (29)) has its origin in the combination of the electrostatic field of the internal charges and the magnetic field generated by their transient currents parallel to the external magnetic field (equation (32)). Therefore, we have found that the longitudinal Casimir momentum is the momentum of the source EM field while the transverse momentum is the momentum of the sourceless vacuum field. In particular, the finding $(P_{1}^{\text{Cas}}) \neq 0$ proves that by modifying the symmetries of space-time it is possible to vary the vacuum expectation value of observable quantities.

The quantum result in equation (36) is linear in $B_0$ and proportional to the fine structure constant, $\alpha$ and to the molecular rotatory power. It is conjectured that this result is universal and model-independent, up to numerical prefactors of order unity which may include relativistic corrections.

The semiclassical approach only applies to the calculation of the transverse Casimir momentum and relies on the

\(^{9}\) In our simplified model the chiral group is free to move within the molecule. The subsequent transfer of kinetic momentum from the chiral group to the rest of the molecule would be accompanied by a redistribution of mechanical energy.

\(^{10}\) $\Delta M_{\text{e}} = -\langle E_{1}^{\text{Lamb}} + E_{1}^{\text{Lamb}}\rangle /\bar{B}_0$ is a shortcut to write the vacuum correction to the magnetization and so is the expression in the integrand of equation (38) for writing the total magnetization. Strictly speaking it should be written $\Delta M_{\text{e}} = -\delta (E_{1}^{\text{Lamb}} + E_{1}^{\text{Lamb}})/\bar{B}_0 + (B_0/2) E_{1}^{\text{Lamb}} + E_{1}^{\text{Lamb}}/\bar{B}_0^2$.\)
non-reciprocity of the spectrum of effective normal modes. However, it fails to incorporate the net effect of the Doppler shift which comes into the microscopical quantum approach and which is seen to dominate largely. The semiclassical result of equation (18) appears as a second order correction to the leading order term of the quantum result.

We have proved that the variation of the kinetic energy of the chromophoric group has its origin in the magnetic Lamb leading order term of the quantum result.

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Appendix A. Rotationally averaged polarizabilities

At leading order in the anisotropy factors, the polarizabilities that enter equation (7) are [35],

\[
\alpha_E = \frac{e^2}{\mu(\omega_0^2 - \omega^2)}, \quad \alpha_M = \frac{4e^2\hbar\omega_0 N_{xyz}}{9\mu\omega^2(4\omega_0^2 - \omega^2)},
\]

\[
\chi = \frac{e^3}{\mu\omega_0^2(\omega_0^2 - \omega^2)} \quad \xi = \frac{e^2\hbar\omega_0(4\omega_0^2 - 3\omega^2)N_{xyz}}{18\mu\omega^2(4\omega_0^2 - \omega^2)},
\]

\[
\beta = \frac{2e^2\hbar C_0 \omega_0^2 (\omega_0^2 + 7\omega_0^2 - 12\omega_0^2)}{\mu^2\omega_0^2(\omega_0^2 - 5\omega_0^2\omega^2 + 4\omega_0^4)},
\]

\[
\gamma = \frac{e^3 C_0 \omega_0^2 (\omega_0^2 + 7\omega_0^2 - 12\omega_0^2)}{\mu^2\omega_0^2(\omega_0^2 - 5\omega_0^2\omega^2 + 4\omega_0^4)},
\]

\[
\xi = \frac{e^2\hbar M_{xyz} 3\omega_0^2 (19\omega_0^2 - 842\omega_0^2\omega_0^2 - 224\omega_0^2\omega_0^4 + 672\omega_0^6)}{15\mu^2\omega_0^2(\omega_0^2 - \omega^2)3(\omega_0^2 - 4\omega_0^2)^5}.
\]

where $M_{xyz}$ and $N_{xyz}$ are dimensionless functions of the anisotropy factors, $M_{xyz} \equiv \eta^3\eta^3\eta^3$, $N_{xyz} \equiv \eta^3\eta^3 + \eta^3\eta^3$.

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