

Casimir-Lifshitz Theory for Cavity Modification of Ground-State Energy

Oleg V. Kotov^{1,2,3,*}, Johannes Feist^{2,3}, Francisco J. García-Vidal^{2,3}, and Timur O. Shegai^{1,†}

¹*Department of Physics, Chalmers University of Technology, 412 96 Göteborg, Sweden*

²*Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain*

³*Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, E-28049 Madrid, Spain*



(Received 4 September 2025; accepted 5 December 2025; published 24 December 2025)

A theory for ground-state modifications of matter embedded in a Fabry-Perot cavity and whose excitations are described as harmonic oscillators is presented. Based on Lifshitz's theory for vacuum energy and employing a Lorentz model for the material permittivity, a nonperturbative macroscopic QED model that accounts for the infinite number of cavity modes with a continuum of their wave vectors was built. Differences from the commonly used single-mode Hopfield Hamiltonian are revealed. The nonresonant role of polaritons in the ground-state energy shift is also demonstrated, showing that the cavity effect is mainly caused by static screening occurring at very low frequencies. The theory allows for a straightforward incorporation of losses and temperature effects.

DOI: [10.1103/v79d-tyy5](https://doi.org/10.1103/v79d-tyy5)

Introduction—Vacuum-induced modifications of molecular properties in a “dark” cavity have recently attracted considerable attention [1]. It is claimed that strong coupling (SC) of electromagnetic (EM) modes to material excitations can modify a range of material properties, including chemical reaction rates [2–6], dielectric constants [7], work functions [8], phase transitions [9,10], ferromagnetism [11], and (super)conductivity [12–18]. It has long been suggested that ultrastrong coupling (USC) of matter to individual cavity modes can modify the system's ground state [19–21]. Vibropolaritonic chemistry is typically realized in Fabry-Perot (FP) cavities by the effect of collective strong coupling with a very large number of molecules and without external driving, i.e., at thermodynamic equilibrium, suggesting that USC effects could be responsible. However, available theoretical approaches do not explain the observed changes under these conditions [22–24]. There is thus a clear need for a theoretical approach that links USC to polariton chemistry and can incorporate the experimentally relevant conditions.

A wide range of quantum optical Hamiltonian approaches has been employed to account for ground-state modifications in the SC and USC regimes [25–27]. However, these methods are typically restricted to a single [19] or a few [28–30] EM modes with a fixed

wave vector, which severely limits their applicability. Furthermore, they treat a cavity as creating new EM modes, instead of taking into account that it primarily rearranges existing ones. The need to subtract the unmodified background leads us to a framework of Casimir-Lifshitz dispersion forces [31,32], which is based on such subtraction and accounts for the infinite number of cavity modes with a continuum of their wave vectors. Starting from the full cavity Hopfield Hamiltonian we derive the exact ground-state energy of oscillators in a cavity matching it to the Casimir-Lifshitz energy with Lorentz permittivity. We regularize infinite sums of polaritonic zero-point energies (ZPEs) by using a Wick rotation to the imaginary frequency axis and subtracting the infinite free-space ZPE. Perturbatively, a similar approach has been previously applied for a single oscillator in a cavity [33,34], leading to the Casimir-Polder energy [34–36]. However, summing up Casimir-Polder interactions for an ensemble of molecules is significantly more challenging. By contrast, the Lifshitz approach, which treats molecules as a homogeneous medium described by a Lorentz dielectric function, allows for an exact, *nonperturbative*, and cost-efficient calculation providing an accurate analytical approximation for the ground-state energy shift. Furthermore, the theory naturally accommodates arbitrary mirror materials, material losses, and finite-temperature effects. A Wick rotation converts all resonant polaritonic features into monotonic functions so that the main contribution to the ground-state energy originates from small imaginary frequencies, which contain information about polaritons, but in a nonresonant way.

Lorentz permittivity and QED Hopfield Hamiltonian—We first consider an infinite resonant medium homogeneously and isotropically filled with atoms or molecules

*Contact author: oleg.kotov@uam.es

†Contact author: timurs@chalmers.se

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International](https://creativecommons.org/licenses/by/4.0/) license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI. Funded by [Bibsam](https://www.bibsam.com/).

having the same resonant frequencies ω_0 and relaxation rates γ . In a linear approximation, they can be treated as harmonic oscillators, and neglecting the interaction between them, the dielectric function of the entire medium for light wavelengths much larger than the distance between the oscillators can be described by the classical Lorentz permittivity:

$$\varepsilon(\omega, g) = 1 + \frac{f\omega_p^2}{\omega_0^2 - \omega^2 - i\omega\gamma} = 1 + \frac{4g^2}{\omega_0^2 - \omega^2 - i\omega\gamma}, \quad (1)$$

where ω_p and f are the collective plasma frequency of the oscillators and the oscillator strength, respectively, and g is a measure of the light-matter coupling.

From a quantum perspective, these Lorentz materials in the lossless limit $\gamma \rightarrow 0$ can be described using the so-called QED Hopfield Hamiltonian [37]:

$$\begin{aligned} \hat{H} = \sum_{k,\lambda} \left[\hbar\omega_k \left(\hat{a}_{k,\lambda}^\dagger \hat{a}_{k,\lambda} + \frac{1}{2} \right) + \hbar\omega_0 \left(\hat{b}_{k,\lambda}^\dagger \hat{b}_{k,\lambda} + \frac{1}{2} \right) \right. \\ \left. + \hbar g_C (\hat{a}_{k,\lambda}^\dagger + \hat{a}_{k,\lambda}) (\hat{b}_{k,\lambda}^\dagger + \hat{b}_{k,\lambda}) + \frac{\hbar g_C^2}{\omega_0} \left(\hat{a}_{k,\lambda}^\dagger + \hat{a}_{k,\lambda} \right)^2 \right], \end{aligned} \quad (2)$$

where the sum is taken over the conserved wave vector k and two polarizations $\lambda = (p, s)$, while $\hat{a}_{k,\lambda}^\dagger$ and $\hat{b}_{k,\lambda}^\dagger$ are the creation operators of the free-space photons ($\omega_k = ck$) and of the collective matter excitations with dispersionless frequency ω_0 , respectively. Importantly, the light-matter interaction strength in this minimal-coupling description is given by $g_C^2 = g^2\omega_0/\omega_k$, and thus is k -dependent, such that the Lorentz permittivity is recovered when calculating the normal modes (*bulk polaritons*) of the QED Hopfield Hamiltonian [see Supplemental Material (SM) Sec. I [38]].

Cavity polaritons—We are interested in analyzing the ground-state energy of a system consisting of the material described by a Lorentz permittivity embedded in an FP cavity. We first analyze the case of FP mirrors made of a perfect electrical conductor (PEC); see Fig. 1(a). For calculating the normal modes of the system, i.e., *cavity polaritons*, we can write a Hopfield-like Hamiltonian [19] similar to that of Eq. (2), but instead of the unbounded light frequency ck , there appear discrete bands of cavity modes, $\omega_{q,n} = c\sqrt{q^2 + (\pi n/L)^2}$, with n denoting the out-of-plane mode number and q being the (continuous) in-plane momentum. In Fig. 1(b), we render the dispersion of the cavity polaritons supported by an FP cavity for the case of $g = 0.2\omega_0$ and $\omega_0 = 2\omega_L$, where $\omega_L \equiv \pi c/L$. At large enough g , many cavity polariton branches arise, which account for the coupling of material excitations to multiple cavity modes.

As discussed below, a single-mode approximation to the cavity Hopfield Hamiltonian is often utilized when dealing

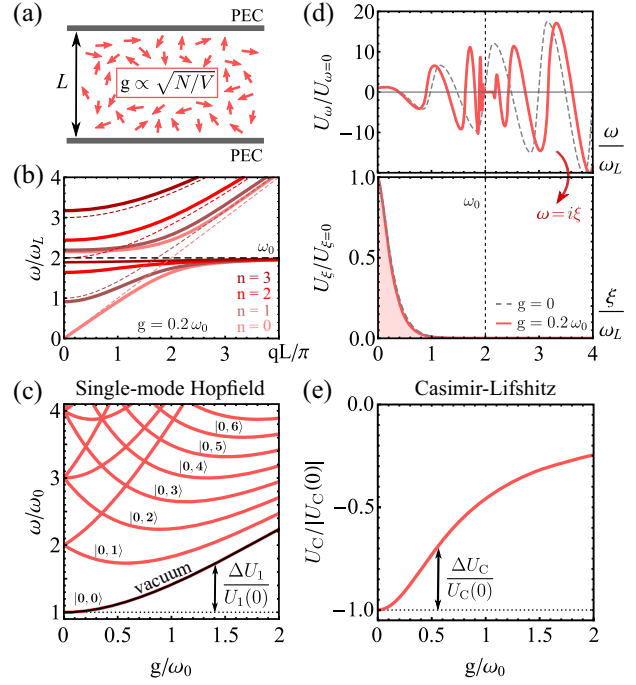


FIG. 1. (a) Sketch of a resonant system consisting of identical harmonic oscillators strongly coupled to the vacuum EM modes in a PEC FP cavity. (b) Cavity polaritons dispersion at $g = 0.2\omega_0$ for $\omega_0 = 2\omega_L$; the empty cavity modes are shown in dashed lines. (c) Single-mode Hopfield Hamiltonian spectrum for the cavity polaritons at normal incidence, fixed polarization, and zero detuning ($\omega_0 = \omega_L$) as a function of g . (d) Real (top) and imaginary (bottom) frequency dependence of the Lifshitz integrand at $T = 0$ in the empty cavity (gray dashed) and polaritonic cavity (red solid). (e) Casimir-Lifshitz energy at $T = 0$ and $\omega_0 = \omega_L$, normalized to the empty cavity case as a function of the coupling energy, g .

with cavity polaritons. Moreover, in some cases, the dispersion of the fundamental ($n = 1$) mode of the cavity is neglected ($q = 0$). In this case, the energy levels of the single-mode Hopfield Hamiltonian are easily written as $\omega_{l,m} = (l + \frac{1}{2})\omega_1^+ + (m + \frac{1}{2})\omega_1^-$, where l and m are non-negative integers and ω_1^\pm are the frequencies of the two polaritons formed by the coupling between the fundamental mode ω_L and ω_0 ; compare Fig. 1(c).

Ground-state energy change: Casimir-Lifshitz versus single-mode Hopfield Hamiltonian—The ground-state energy, i.e., ZPE of a material embedded in an FP cavity, can be found from the full cavity Hopfield-like Hamiltonian and expressed as the half-sum of the FP cavity polaritons:

$$U(g, L) = \frac{1}{2} \sum_{a,q,\lambda} \hbar\omega_a(a, q, g, L), \quad (3)$$

where the sum involves the discrete polaritonic state index a (with typically two polaritons for each mode index n), the

in-plane wave vectors q , and the polarization λ . The sum over the conserved wave vectors q can be expressed through an integral with the corresponding density of states. Equation (3) already accounts for both photonic and matter oscillators' ZPEs, as well as their coupling term. However, to obtain a finite value from this infinite energy, one needs to subtract the ZPE of the uncoupled system. Direct subtraction, $U(g, L) - U(0, L)$, may still diverge (see SM Sec. II [38]), while Casimir-type subtraction of the ZPE within the same volume but using the continuous dispersion relation obtained outside a cavity, $U_C(g, L) = U(g, L) - U_\infty(g, L)$, leads to a well-defined energy. Therefore, in order to get the cavity-induced ground-state energy shift due to light-matter coupling, we calculate the difference between Casimir energies as the coupling is turned on: $\Delta U_C = U_C(g, L) - U_C(0, L)$.

A direct calculation of the ground-state energies by summing over the real frequencies of all cavity polaritons, as written in Eq. (3), does not converge. The key approach that we take to circumvent this problem was developed by Barash and Ginzburg [46–48], which also naturally allows for treating dissipative matter oscillators [$\gamma > 0$ in Eq. (1)] and nonperfect mirrors. This approach establishes a fundamental connection between the equilibrium average energy (ZPE at zero temperature) of a system of damped oscillators and the dispersion relation for the eigenmodes of that system. Barash-Ginzburg theory proves that the polaritonic ZPE in a cavity, $U_C(g, L)$, corresponds to the standard expression for the Lifshitz energy per unit area S (see SM [38]), which at zero temperature is given by [48,49]

$$\frac{U_C(g, L)}{S} = \frac{\hbar}{4\pi^2} \int_0^\infty q dq \int_0^\infty d\xi \sum_{\lambda=p,s} \ln(1 - r_\lambda^- r_\lambda^+ e^{-2k_z L}), \quad (4)$$

where $k_z = \sqrt{q^2 + \epsilon(i\xi, g)\xi^2/c^2}$ and $r_\lambda^\pm(q, i\xi, g)$ are the Fresnel reflection coefficients of the top and bottom mirrors (including the substrate). Notice that, for an empty PEC cavity ($r_\lambda^- r_\lambda^+ = 1$, $\epsilon = 1$), Eq. (4) gives the well-known Casimir energy $U_C(0, L) = -\hbar c \pi^2 L^{-3}/720$ [50]. In Eq. (4), the integration is performed over imaginary frequencies $\omega = i\xi$ (see SM Sec. III A [38]), which, together with the subtraction of the cavity-free limit, eliminates the divergence of Eq. (3). Importantly, Eq. (4) contains the Lorentz permittivity, Eq. (1), since it is derived from Eq. (3) with cavity polaritons whose dispersion relation is governed by this specific permittivity.

At real frequencies, the Lifshitz integrand U_ω [given by Eq. (4) evaluated after wave vector integration but before frequency integration] behaves similarly to the local density of photonic states in the cavity. It exhibits periodic sign changes, has a polaritonic gap, and (for PEC mirrors) grows without limit with frequency [51]; see top panel of Fig. 1(d). This behavior explains why a direct calculation

of $U_C(g, L)$ based on Eq. (3) does not converge and why including more cavity modes within a few-mode approximation to the Hopfield Hamiltonian can change the answer even qualitatively without necessarily improving agreement with the correct result [28,52].

Wick rotation to imaginary frequencies eliminates not only the divergence but also all resonant features, making the integrand U_ξ smooth, monotonic, and rapidly decaying; compare bottom panel of Fig. 1(d). Although it encompasses all of the information about the polaritons, their visual impact compared to $g = 0$ is barely noticeable. The integrand decays rapidly from its maximum at $\xi = 0$, where for PEC at $T = 0$ it is given by $U_{\xi=0} = -\zeta(3)/(8L^2\pi^2)$, with approximately 99% of the total energy originating from imaginary frequencies smaller than the fundamental cavity mode frequency ω_L . The nonresonant behavior of U_ξ leads to a monotonic dependence of the Casimir-Lifshitz energy U_C on g , as shown in Fig. 1(e).

For PEC mirrors at $T = 0$, it is feasible to obtain an analytical approximation for the cavity-induced change of the ground-state energy. By taking the screening factor in the static limit, $1/\sqrt{\epsilon(i\xi = 0, g)}$, out of the integral in Eq. (4), the relative Casimir energy change within what we call *static screening approximation* (SSA) can be written as (see SM Sec. IV [38])

$$\left. \frac{\Delta U_C}{U_C(0)} \right|_{\text{stat}} \approx 1 - \frac{1}{\sqrt{\epsilon(0, g)}} = 1 - \frac{1}{\sqrt{1 + 4g^2/\omega_0^2}}. \quad (5)$$

As shown in Fig. 2(a), at $T = 0$ the SSA reproduces the exact Lifshitz solution extremely well for the whole range of g/ω_0 , confirming the key role of the zero-frequency limit for the ground-state energy shift. This is reminiscent of earlier results showing that the cavity-mediated interaction between low-energy excitations reduces to the electrostatic limit [53–56].

As commented above, many works have employed a single-mode Hopfield Hamiltonian to study cavity-induced changes in ground-state energy. Within this single-mode approximation, the energy shift can be calculated as the difference between the polaritonic ZPE and the ZPE of the uncoupled system [19,52]: $\Delta U_1 = \hbar(\omega_1^+ + \omega_1^- - \omega_0 - \omega_L)/2$. Unlike the Casimir-Lifshitz energy, the single-mode Hopfield ZPE does not contain the free-space subtraction and does not scale with the mirror area as no integration over parallel wave vectors is performed. However, when considering the relative change of the ground state energy, a quantitative comparison between Casimir-Lifshitz and single-mode Hopfield energy shifts becomes possible, as the area dependence in the Casimir energy cancels out. In the limit $g \ll \omega_0$, the single-mode Hopfield relative energy changes simplifies to

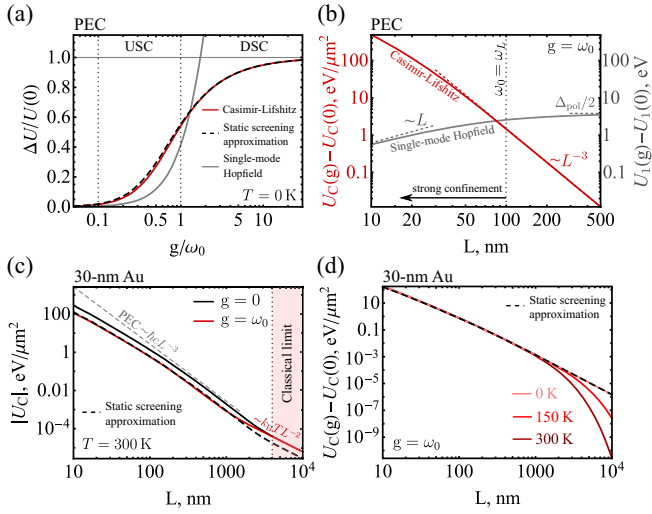


FIG. 2. (a) Relative change of the ground-state energy vs coupling g in a PEC cavity at $T = 0$ K and $L = 100$ nm according to Lifshitz (red) and single-mode Hopfield (gray) approaches. The static screening approximation (SSA) is shown in dashed lines. USC and deep strong coupling (DSC) denote ultrastrong and deep strong coupling regimes, respectively. (b) Absolute change of the ground-state energy vs L at $T = 0$ K, with the left axis for Lifshitz and the right one for single-mode Hopfield solutions. (c) Casimir-Lifshitz energy of the cavity with 30-nm gold mirrors on a glass substrate at $T = 300$ K without (black) and with (red) a medium (with bulk coupling $g = \omega_0$). SSA results are depicted by dashed lines. (d) Absolute change in ground-state energy at different temperatures. SSA works perfectly at $T = 0$ K, as expected. In all plots ω_0 is tuned to the main mode of $L = 100$ nm cavity ($\omega_0 = \omega_{L=100 \text{ nm}}$).

$$\frac{\Delta U_1}{U_1(0)} = \frac{2g^2}{(\omega_0 + \omega_L)^2} + O(g^4) \quad (6)$$

For a PEC cavity at $T = 0$, a detailed comparison between the results of the Lifshitz-Lorentz approach and those obtained with the single-mode Hopfield Hamiltonian is rendered in panels (a) and (b) of Fig. 2. For the relative change of the ground-state energy as a function of g , at $g \ll \omega_0$, both curves grow quadratically but with very different prefactors. However, already in the USC regime (at the inflection point $g \approx 0.4\omega_0$), the Lifshitz curve begins to bend toward saturation at $g \gg \omega_0$, whereas the single-mode solution in the DSC regime shows unbounded linear growth [Fig. 2(a)]. The Lifshitz-Lorentz approach provides a physically meaningful saturation at the high- g limit, where $\epsilon(g)$ becomes so large that it fully screens the Lifshitz energy, effectively suppressing any further modifications. This limit corresponds to a very large number of oscillators, analogous to the thermodynamic limit $N \gg 1$ in microscopic analyses [57]. In this regime, the ground state of the harmonic oscillators cannot be modified through coupling to vacuum modes by more than the initial vacuum energy contained within them, $\Delta U/U(0) \leq 1$.

For polaritonic chemistry phenomena, it is also relevant to know the absolute change in ground-state energy. Comparing ΔU from both approaches on the same plot is valuable as it reveals their qualitatively different behavior with respect to L . Unlike the relative energy difference, ΔU obeys a fundamentally different L scaling. The single-mode Hopfield ZPE increases linearly with L in tightly confined cavities ($L \ll \pi c/\omega_0$) and saturates at a constant value determined by the polaritonic gap $\Delta_{\text{pol}}/2$ in large ones [Fig. 2(b)], which is unphysical, since $L \rightarrow \infty$ corresponds to the absence of a cavity (see SM Sec. III C [38]). By contrast, the Lifshitz energy rapidly decreases with increasing L , reaching its static limit scaling with L^{-3} already around $L = 50$ nm.

Temperature effects and non-PEC mirrors—Lifshitz’s formalism, in contrast to the single-mode Hopfield Hamiltonian, can easily incorporate the effects of temperature and nonperfect cavity mirrors made of real materials. At a finite temperature T , the integral over imaginary frequencies in Eq. (4) is replaced by a sum over Matsubara frequencies $\xi_j = 2\pi j k_B T/\hbar$, where k_B is the Boltzmann constant, $j = 0, 1, 2, \dots$, and the term with $j = 0$ is multiplied by $1/2$. Non-PEC mirrors can be accounted for in Eq. (4) by evaluating their associated Fresnel coefficients, $r_{p,s}^\pm$. At sufficiently high temperatures or distances L , classical thermal fluctuations completely dominate quantum ones (see SM Sec. III B [38]). Instead of the Casimir power law $\propto \hbar c L^{-3}$, in the classical limit the energy scales as $\propto k_B T L^{-2}$ [31, 58, 59]. In this limit, only the $\xi = 0$ contribution remains. Moreover, in this effectively electrostatic limit, the reflection becomes perfect not only for PECs but even for realistic Drude mirrors (although the reflection for s polarization vanishes for $\xi = 0$), and the contribution of $\epsilon(i\xi, g)$ completely vanishes. This can be clearly seen in Figs. 2(c) and 2(d), which show the Lifshitz energy for gold mirrors (Drude model) at different temperatures. $U_C(0)$ deviates from the PEC L^{-3} scaling at $L < 1$ μm but reaches a similar classical limit L^{-2} scaling at $L \approx 4$ μm. On the other hand, $U_C(g)$ merges with $U_C(0)$ when they both reach the classical limit [Fig. 2(c)]. This shows a complete absence of vacuum-induced energy shifts in mid-infrared FP cavities at room temperature [Fig. 2(d)].

Casimir-Lifshitz energy and cavity polaritons—Figure 3(a) shows the absolute value of Casimir-Lifshitz energy for varying couplings, calculated with Eq. (4) for realistic FP cavities with gold mirrors and molecular oscillators in water. When the cavity is tuned to the oscillator resonance, $\omega_0 = \omega_L$, we do not observe a resonant behavior of the vacuum energy, similar to the nonresonant effect of Casimir-Polder shifts on chemical reactions [60]. Instead, it is gradually suppressed with increasing g , whereas the transmission spectra display typical polariton splitting with USC and even DSC features appearing at progressively increasing couplings; see the inset in Fig. 3(a). Thus, polaritons are indeed present, but they do not exert a

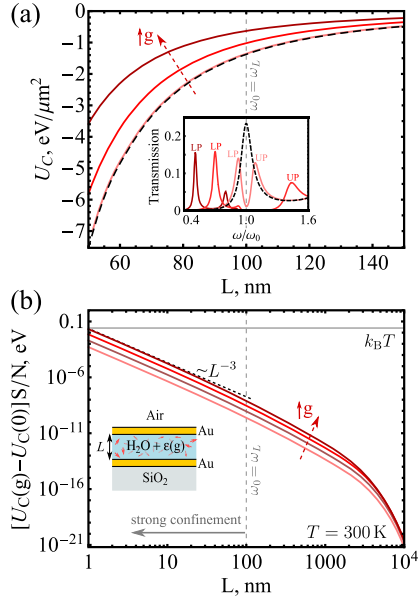


FIG. 3. (a) Nonresonant behavior of the Casimir-Lifshitz energy for a gold cavity on a glass substrate filled with molecules floating in water at room temperature (see the sketch). Different concentrations of molecules leads to g/ω_0 varying from 0 (black dashed) to 0.1, 0.5, 1 (light to dark red), where ω_0 equals the main mode of 100-nm-cavity. The inset shows the corresponding transmission spectrum with the resonant splittings having USC and DSC features. (b) For the same system, the change of the Lifshitz energy per molecule, showing a similar scaling law as nonretarded Casimir-Polder energy at small L and vanishing of the energy shift at large L .

resonant effect on the ground-state energy. This prediction could be tested experimentally, e.g., by extracting the Casimir energy from the total equilibrium potential of self-assembled microcavities [61–63] or by examining the corresponding pressure using a liquid-phase AFM [64–66] (see SM Sec. V [38]). As a simple illustrative estimate, we use Eq. (5), which at $g \ll \omega_0$ yields $\Delta U/U(0) \approx 2 g^2/\omega_0^2$, thus leading to a 2% relative change at $g = 0.1\omega_0$.

Given that chemical processes usually occur at the level of individual molecules, a key characteristic of polaritonic chemistry is the ground-state change per molecule [67]. Assuming that all N molecules contribute independently, we can simply divide the Casimir-Lifshitz energy by the number of molecules. For gold mirrors, the Lifshitz energy per molecule in the van der Waals limit is $U_C S/N = U_C/(\rho L) \propto L^{-3}$, where ρ is the concentration of the molecules. The same scaling law is known for the nonretarded Casimir-Polder (London) energy [68]. Notice that even in extremely small nanocavities ($L < 10$ nm) the energy corrections in the USC and even DSC regimes are smaller than $k_B T$ at room temperature; see Fig. 3(b).

To conclude, using Barash-Ginzburg theory to regularize the infinite sum of polaritonic zero-point energies, we have derived the exact ground-state energy change of a material

characterized by a Lorentz permittivity when embedded in a Fabry-Perot cavity. In this way, our Casimir-Lifshitz calculation provides the ground-state energy associated with the full cavity QED Hopfield Hamiltonian. We show that the cavity-modification is mainly governed by the quasistatic response and that cavity polaritons do not exert a resonant effect on the ground-state energy. We have compared the results of this full calculation with those obtained with the commonly used single-mode Hopfield Hamiltonian, showing the severe limitations of this approach. We have also analyzed temperature effects and incorporated mirror losses. To test our findings, we suggest using Casimir measurements in Fabry-Perot cavities to experimentally probe ground-state modifications, thus bridging Casimir and polariton physics.

Acknowledgments—The authors acknowledge fruitful discussions with D.G. Baranov, F. Lindel, S. Y. Buhmann, R. Podgornik, and V.M. Mostepanenko. This work was supported by the Swedish Research Council (VR project, Grant No. 202203347), the Knut and Alice Wallenberg Foundation (Grant No. 2019.0140), the Olle Engkvist Foundation (Grant No. 211-0063), and Chalmers Area of Advance Nano. We also acknowledge financial support by the Spanish Ministerio de Ciencia y Universidades—Agencia Estatal de Investigación through Grants No. PID2021-125894NB-I00, No. PID2024-161142NB-I00, No. EUR2023-143478, and No. CEX2023-001316-M through the María de Maeztu program for Units of Excellence in R&D.

Data availability—The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

- [1] F. J. Garcia-Vidal, C. Ciuti, and T. W. Ebbesen, Manipulating matter by strong coupling to vacuum fields, *Science* **373**, eabd0336 (2021).
- [2] A. Thomas, J. George, A. Shalabney, M. Dryzhakov, S. J. Varma, J. Moran, T. Chervy, X. Zhong, E. Devaux, C. Genet, J. A. Hutchison, and T. W. Ebbesen, Ground-state chemical reactivity under vibrational coupling to the vacuum electromagnetic field, *Angew. Chem., Int. Ed. Engl.* **55**, 11462 (2016).
- [3] A. Thomas, L. Lethuillier-Karl, K. Nagarajan, R. M. A. Vergauwe, J. George, T. Chervy, A. Shalabney, E. Devaux, C. Genet, J. Moran, and T. W. Ebbesen, Tilting a ground-state reactivity landscape by vibrational strong coupling, *Science* **363**, 615 (2019).
- [4] W. Ahn, J. F. Triana, F. Recabal, F. Herrera, and B. S. Simpkins, Modification of ground-state chemical reactivity via light–matter coherence in infrared cavities, *Science* **380**, 1165 (2023).

- [5] F. Verdelli, Y.-C. Wei, K. Joseph, M. S. Abdelkhalik, M. Goudarzi, S. H. C. Askes, A. Baldi, E. W. Meijer, and J. Gomez Rivas, Polaritonic chemistry enabled by non-local metasurfaces, *Angew. Chem., Int. Ed. Engl.* **63**, e202409528 (2024).
- [6] Z. T. Brawley, S. Pannir-Sivajothi, J. E. Yim, Y. R. Poh, J. Yuen-Zhou, and M. Sheldon, Vibrational weak and strong coupling modify a chemical reaction via cavity-mediated radiative energy transfer, *Nat. Chem.* **17**, 439 (2025).
- [7] T. Fukushima, S. Yoshimitsu, and K. Murakoshi, Inherent promotion of ionic conductivity via collective vibrational strong coupling of water with the vacuum electromagnetic field, *J. Am. Chem. Soc.* **144**, 12177 (2022).
- [8] J. A. Hutchison, A. Liscio, T. Schwartz, A. Canaguier-Durand, C. Genet, V. Palermo, P. Samorì, and T. W. Ebbesen, Tuning the work-function via strong coupling, *Adv. Mater.* **25**, 2481 (2013).
- [9] S. Wang, A. Mika, J. A. Hutchison, C. Genet, A. Jouaiti, M. W. Hosseini, and T. W. Ebbesen, Phase transition of a perovskite strongly coupled to the vacuum field, *Nanoscale* **6**, 7243 (2014).
- [10] G. Jarc, S. Y. Mathengattil, A. Montanaro, F. Giusti, E. M. Rigoni, R. Sergo, F. Fassiolli, S. Winnerl, S. Dal Zilio, D. Mihailovic *et al.*, Cavity-mediated thermal control of metal-to-insulator transition in 1T-TaS₂, *Nature (London)* **622**, 487 (2023).
- [11] A. Thomas, E. Devaux, K. Nagarajan, G. Rogez, M. Seidel, F. Richard, C. Genet, M. Drillon, and T. W. Ebbesen, Large enhancement of ferromagnetism under a collective strong coupling of YBCO nanoparticles, *Nano Lett.* **21**, 4365 (2021).
- [12] E. Orgiu, J. George, J. A. Hutchison, E. Devaux, J. F. Dayen, B. Doudin, F. Stellacci, C. Genet, J. Schachenmayer, C. Genes, G. Pupillo, P. Samorì, and T. W. Ebbesen, Conductivity in organic semiconductors hybridized with the vacuum field, *Nat. Mater.* **14**, 1123 (2015).
- [13] M. A. Sentef, M. Ruggenthaler, and A. Rubio, Cavity quantum-electrodynamical polaritonically enhanced electron-phonon coupling and its influence on superconductivity, *Sci. Adv.* **4**, eaau6969 (2018).
- [14] A. Thomas, E. Devaux, K. Nagarajan, T. Chervy, M. Seidel, D. Hagenmüller, S. Schütz, J. Schachenmayer, C. Genet, G. Pupillo *et al.*, Exploring superconductivity under strong coupling with the vacuum electromagnetic field, *J. Chem. Phys.* **162**, 134701 (2025).
- [15] G. Moddel, A. Weerakkody, D. Doroski, and D. Bartusiak, Casimir-cavity-induced conductance changes, *Phys. Rev. Res.* **3**, L022007 (2021).
- [16] F. Appugliese, J. Enkner, G. L. Paravicini-Bagliani, M. Beck, C. Reichl, W. Wegscheider, G. Scalari, C. Ciuti, and J. Faist, Breakdown of topological protection by cavity vacuum fields in the integer quantum hall effect, *Science* **375**, 1030 (2022).
- [17] S. Kumar, S. Biswas, U. Rashid, K. S. Mony, G. Chandrasekharan, F. Mattiotti, R. M. Vergauwe, D. Hagenmüller, V. Kaliginedi, and A. Thomas, Extraordinary electrical conductance through amorphous nonconducting polymers under vibrational strong coupling, *J. Am. Chem. Soc.* **146**, 18999 (2024).
- [18] I. Keren, T. A. Webb, S. Zhang, J. Xu, D. Sun, B. S. Kim, D. Shin, S. S. Zhang, J. Zhang, G. Pereira *et al.*, Cavity-altered superconductivity, [arXiv:2505.17378](https://arxiv.org/abs/2505.17378).
- [19] C. Ciuti, G. Bastard, and I. Carusotto, Quantum vacuum properties of the intersubband cavity polariton field, *Phys. Rev. B* **72**, 115303 (2005).
- [20] P. Forn-Díaz, L. Lamata, E. Rico, J. Kono, and E. Solano, Ultrastrong coupling regimes of light-matter interaction, *Rev. Mod. Phys.* **91**, 025005 (2019).
- [21] A. Frisk Kockum, A. Miranowicz, S. De Liberato, S. Savasta, and F. Nori, Ultrastrong coupling between light and matter, *Nat. Rev. Phys.* **1**, 19 (2019).
- [22] T. E. Li, B. Cui, J. E. Subotnik, and A. Nitzan, Molecular polaritonics: Chemical dynamics under strong light-matter coupling, *Annu. Rev. Phys. Chem.* **73**, 43 (2022).
- [23] J. Fregoni, F. J. Garcia-Vidal, and J. Feist, Theoretical challenges in polaritonic chemistry, *ACS Photonics* **9**, 1096 (2022).
- [24] B. Xiang and W. Xiong, Molecular polaritons for chemistry, photonics and quantum technologies, *Chem. Rev.* **124**, 2512 (2024).
- [25] A. Mandal, M. A. Taylor, B. M. Weight, E. R. Koessler, X. Li, and P. Huo, Theoretical advances in polariton chemistry and molecular cavity quantum electrodynamics, *Chem. Rev.* **123**, 9786 (2023).
- [26] M. Ruggenthaler, D. Sidler, and A. Rubio, Understanding polaritonic chemistry from ab initio quantum electrodynamics, *Chem. Rev.* **123**, 11191 (2023).
- [27] J. J. Foley, IV, J. F. McTague, and A. E. DePrince, III, Ab initio methods for polariton chemistry, *Chem. Phys. Rev.* **4**, 041301 (2023).
- [28] A. Mandal, D. Xu, A. Mahajan, J. Lee, M. Delor, and D. R. Reichman, Microscopic theory of multimode polariton dispersion in multilayered materials, *Nano Lett.* **23**, 4082 (2023).
- [29] F. Herrera and W. L. Barnes, Multiple interacting photonic modes in strongly coupled organic microcavities, *Phil. Trans. R. Soc. A* **382**, 20230343 (2024).
- [30] D. Sidler, T. Schnappinger, A. Obzhairov, M. Ruggenthaler, M. Kowalewski, and A. Rubio, Unraveling a cavity-induced molecular polarization mechanism from collective vibrational strong coupling, *J. Phys. Chem. Lett.* **15**, 5208 (2024).
- [31] E. M. Lifshitz, The theory of molecular attractive forces between solids, *Sov. Phys. JETP* **2**, 73 (1956).
- [32] I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii, General theory of van der Waals' forces, *Sov. Phys. Usp.* **4**, 153 (1961).
- [33] G. Barton, Quantum electrodynamics of spinless particles between conducting plates, *Proc. R. Soc. A* **320**, 251 (1970).
- [34] R. Sáez-Blázquez, D. de Bernardis, J. Feist, and P. Rabl, Can we observe nonperturbative vacuum shifts in cavity QED?, *Phys. Rev. Lett.* **131**, 013602 (2023).
- [35] H. B. Casimir and D. Polder, The influence of retardation on the London-van der Waals forces, *Phys. Rev.* **73**, 360 (1948).
- [36] S. Y. Buhmann, *Dispersion Forces I: Macroscopic Quantum Electrodynamics and Ground-State Casimir, Casimir-Polder and van der Waals Forces*, Vol. 247 (Springer, New York, 2013).

- [37] J. Hopfield, Theory of the contribution of excitons to the complex dielectric constant of crystals, *Phys. Rev.* **112**, 1555 (1958).
- [38] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/v79d-tty5>, which includes Refs. [39–45], for the derivation of the static screening approximation, the Lorentz permittivity from the Hopfield Hamiltonian, Lifshitz energy from the Hopfield's ZPE, key aspects of Casimir calculations, and possible experimental verification.
- [39] A. Canales, D. G. Baranov, T. J. Antosiewicz, and T. Shegai, Abundance of cavity-free polaritonic states in resonant materials and nanostructures, *J. Chem. Phys.* **154**, 024701 (2021).
- [40] B. Huttner and S. M. Barnett, Quantization of the electromagnetic field in dielectrics, *Phys. Rev. A* **46**, 4306 (1992).
- [41] N. Van Kampen, B. Nijboer, and K. Schram, On the macroscopic theory of van der Waals forces, *Phys. Lett.* **26A**, 307 (1968).
- [42] V. Parsegian and B. Ninham, Application of the Lifshitz theory to the calculation of van der Waals forces across thin lipid films, *Nature (London)* **224**, 1197 (1969).
- [43] P. W. Milonni, *The Quantum Vacuum: An Introduction to Quantum Electrodynamics* (Academic Press, New York, 2013).
- [44] M. Bordag, G. L. Klimchitskaya, U. Mohideen, and V. M. Mostepanenko, *Advances in the Casimir Effect*, Vol. 145 (Oxford University Press, Oxford, 2009).
- [45] A. W. Rodriguez, F. Capasso, and S. G. Johnson, The Casimir effect in microstructured geometries, *Nat. Photonics* **5**, 211 (2011).
- [46] Y. S. Barash and V. Ginzburg, Contribution to electrodynamic theory of van der Waals forces between macroscopic bodies, *JETP Lett.* **15**, 403 (1972).
- [47] Y. S. Barash and V. L. Ginzburg, Electromagnetic fluctuations in matter and molecular (van-der-Waals) forces between them, *Sov. Phys. Usp.* **18**, 305 (1975).
- [48] Y. S. Barash and V. Ginzburg, Electromagnetic fluctuations and molecular forces in condensed matter, in *Modern Problems in Condensed Matter Sciences*, Vol. 24 (Elsevier, New York, 1989), pp. 389–457.
- [49] M. Bordag, G. L. Klimchitskaya, U. Mohideen, and V. M. Mostepanenko, *Advances in the Casimir Effect* (Oxford University Press, Oxford, 2015).
- [50] H. B. Casimir, On the attraction between two perfectly conducting plates, *Proc. K. Ned. Akad. Wet.* **51**, 793 (1948).
- [51] M. T. H. Reid, A. W. Rodriguez, and S. G. Johnson, Fluctuation-induced phenomena in nanoscale systems: Harnessing the power of noise, *Proc. IEEE* **101**, 531 (2013).
- [52] D. G. Baranov, B. Munkhbat, E. Zhukova, A. Bisht, A. Canales, B. Rousseaux, G. Johansson, T. J. Antosiewicz, and T. Shegai, Ultrastrong coupling between nanoparticle plasmons and cavity photons at ambient conditions, *Nat. Commun.* **11**, 2715 (2020).
- [53] P.-A. Pantazopoulos, J. Feist, A. Kamra, and F. J. García-Vidal, Electrostatic nature of cavity-mediated interactions between low-energy matter excitations, *Phys. Rev. B* **109**, L201408 (2024).
- [54] C. J. Sánchez Martínez, F. Lindel, F. J. García-Vidal, and J. Feist, General theory of cavity-mediated interactions between low-energy matter excitations, *J. Chem. Phys.* **161**, 194303 (2024).
- [55] G. M. Andolina, A. De Pasquale, F. M. D. Pellegrino, I. Torre, Frank H. L. Koppens, and M. Polini, Amperean superconductivity cannot be induced by deep subwavelength cavities in a two-dimensional material, *Phys. Rev. B* **109**, 104513 (2024).
- [56] R. Riolo, A. Tomadin, G. Mazza, R. Asgari, A. H. MacDonald, and M. Polini, Tuning Fermi liquids with polaritonic cavities, *Proc. Natl. Acad. Sci. U.S.A.* **122**, e2407995122 (2025).
- [57] D. Novokreschenov, A. Kudlis, I. Iorsh, and I. V. Tokatly, Quantum electrodynamical density functional theory for generalized Dicke model, *Phys. Rev. B* **108**, 235424 (2023).
- [58] J. Mehra, Temperature correction to the Casimir effect, *Physica (Utrecht)* **37**, 145 (1967).
- [59] J. Schwinger, L. L. DeRaad Jr, and K. A. Milton, Casimir effect in dielectrics, *Ann. Phys. (N.Y.)* **115**, 1 (1978).
- [60] J. Galego, C. Climent, F. J. Garcia-Vidal, and J. Feist, Cavity Casimir-Polder forces and their effects in ground-state chemical reactivity, *Phys. Rev. X* **9**, 021057 (2019).
- [61] B. Munkhbat, A. Canales, B. Küçüköz, D. G. Baranov, and T. O. Shegai, Tunable self-assembled Casimir microcavities and polaritons, *Nature (London)* **597**, 214 (2021).
- [62] B. Küçüköz, O. V. Kotov, A. Canales, A. Y. Polyakov, A. V. Agrawal, T. J. Antosiewicz, and T. O. Shegai, Quantum trapping and rotational self-alignment in triangular Casimir microcavities, *Sci. Adv.* **10**, eadn1825 (2024).
- [63] M. Hořková, O. V. Kotov, B. Küçüköz, C. J. Murphy, and T. O. Shegai, Casimir self-assembly: A platform for measuring nanoscale surface interactions in liquids, *Proc. Natl. Acad. Sci. U.S.A.* **122**, e2505144122 (2025).
- [64] S. Biggs and P. Mulvaney, Measurement of the forces between gold surfaces in water by atomic force microscopy, *J. Chem. Phys.* **100**, 8501 (1994).
- [65] J. N. Munday and F. Capasso, Precision measurement of the Casimir-Lifshitz force in a fluid, *Phys. Rev. A* **75**, 060102 (R) (2007).
- [66] J. N. Munday, F. Capasso, and V. A. Parsegian, Measured long-range repulsive Casimir-Lifshitz forces, *Nature (London)* **457**, 170 (2009).
- [67] L. A. Martínez-Martínez, R. F. Ribeiro, J. Campos-González-Angulo, and J. Yuen-Zhou, Can ultrastrong coupling change ground-state chemical reactions?, *ACS Photonics* **5**, 167 (2018).
- [68] S. Buhmann, *Dispersion Forces II: Many-Body Effects, Excited Atoms, Finite Temperature and Quantum Friction*, Vol. 248 (Springer, New York, 2013).