Cavity-Induced Quantum Interference and Collective Interactions in van der Waals Systems

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The central topic of this letter is to show that light-matter hybridization not only gives rise to novel dynamic responses but can also modify intermolecular interactions and induce new structural order. Using the van der Waals (vdW) system in an optical cavity as an example, we predict the effects of interference and collectivity in cavity-induced many-body dispersion interactions. Specifically, the leading order correction due to cavity-induced quantum fluctuations leads to 3-body and 4body vdW interactions, which can align intermolecular vectors and are not pairwise additive. In addition, the cavity-induced dipole leads to a single-molecule energy shift that aligns individual molecules, and a pair-wise interaction that scales as R^{-3} instead of the standard R^{-6} distance scaling. The coefficients of all these cavityinduced corrections depend on the cavity frequency and are renormalized by the effective Rabi frequency, which in turn depends on the particle density. Finally, we study the interaction of the vdW system in a cavity with an external object and find a significant enhancement in the interaction range due to modified distance scaling laws. These theoretical predictions suggest the possibility of cavity-induced nematic or smectic order and may provide an essential clue to understand intriguing phenomena observed in optical cavities, such as strongly-modified ground-state reactivity, ion transport and solvent polarity.

The van der Waals (vdW) interaction, also known as dispersion force, is a fundamental force between any pair of atoms or molecules and plays an important role in physics and chemistry.^{1,2} As illustrated in Fig. 1a, London demonstrated that quantum fluctuations in transition dipoles lead to a long-range pairwise attraction that scales with the distance as R^{-6} .^{3,4} The microscopic interpretation suggests that the vdW attraction can be manipulated by strong electromagnetic fields, which can be achieved collectively in optical cavities.^{5–8} Indeed, recent simulations of H_2 molecular systems^{9,10} have demonstrated this possibility and suggested the exciting possibility of modifying the structure of molecular systems by tuning the light-matter coupling parameters. These numerical studies of many-body systems are computationally expensive, whereas theoretical analysis has mostly been limited to pairwise interactions.^{11,12} In this paper, we aim to reveal interference effects in cavityinduced many-body interactions and predict the scaling relations of the resulting collective vdW interaction.

This study is directly motivated by intriguing phenomena observed in optical cavities, including the significant modification of ground-state reactivity, ion transport, and solvent polarity, which require better mechanistic understandings.^{6–8} Most theoretical studies have focused on polariton dynamics in unperturbed molecular configurations but cannot fully explain the cavity-catalyzed reactions^{13–19} and other experiments. As proposed in this and related studies, the collective vdW interactions in optical cavities can potentially modify the structure of vdW systems and change their thermodynamics and dynamic response. Thus, our predictions can shed new light on how to understand and control the unusual properties of condensed phase cavity systems.

Model and basis sets We consider an ensemble of two-level systems or spins in an optical cavity. Each spin represents a ground state and an excited state, which are coupled to the cavity mode. Here, we consider the vdW system as electronic, but the same formalism applies to vibrations, rotations, and other degrees of freedom. The molecular systems interact via the dipole-dipole interactions (DDI) between fluctuating dipoles, which give rise to the vdW attraction. The light-matter (LM) interaction in the cavity is described by the Pauli-Fierz (PF) Hamiltonian,²⁰ which contains the dipole self-energy (DSE) and counter-rotating-wave (CRW) terms. Thus, the overall Hamiltonian is given as

$$H = H_{TCM} + H_{CRW} + H_{DSE} + H_{DDI}, \tag{1}$$

where H_{TCM} is the Hamiltonian of the Tavis-Cummings model (TCM), and other terms are defined later when they are evaluated. Explicitly, the TCM Hamiltonian reads $H_{TCM} = E_c a^+ a^+$ $E_m \sum_i \sigma_i^+ \sigma_i^- + H_{RWA}$ where a and a^+ are the lowering and raising operators of the cavity photon, σ_i^- and σ_i^+ are the lowering and raising operators for the spin associated with the i-th molecule, and E_c and E_m are their respective energies. The TCM adopts the rotating wave approximation (RWA) for the LM interaction, $H_{RWA} = g(\Sigma^+ a + \Sigma^- a^+)$, where g is the LM coupling strength, $\Sigma^+ = \sum_i \sigma_i^+$ and $\Sigma^- = \sum_i \sigma_i^-$.

The vdW attraction arises from the energy shift on the ground state due to the DDI and involves zero or double quantum transitions. Therefore, it suffices to consider the eigenstates of the TCM on the ground and double-excitation manifolds and evaluate other terms in Eq. (1) via perturbation. Following the detailed derivation given in the Supporting Information (SI), we first construct the collective particle states and then diagonalize H_{RWA} in each excitation manifolds to obtain LM hybrid states. Some aspects of the basis set construction and its application to cavity polaritons can be found in literature.^{21–26}

Dipole-dipole interaction (DDI) To begin, we introduce the dipole-dipole interaction $H_{DDI} = -\sum_{i>j} \sigma_i T_{ij} \sigma_j$, where $\sigma = \sigma^+ + \sigma^-$ and T is the projection of the DDI tensor in the polarization direction of the cavity field. Since two particle operators are involved, H_{DDI} connects the ground state and the double-excitation manifold. For simplicity, we use M_2 to denote the double-excitation manifold, i.e., M_2 ; λ to specify an eigen-state in M_2 ; and $E_{2,\lambda}$ to specify the corresponding eigen-energy. Then, the second-order perturbation calculation of the ground state energy gives

$$E_{DDI} = -\sum_{\lambda} \frac{|\langle M_{2,\lambda} | H_{DDI} | G \rangle|^2}{E_{2,\lambda}} = -\sum_{\lambda} \frac{|\langle M_{2,\lambda} | H_{DDI} | G \rangle|^2}{2\omega} - \sum_{P_2} \left(\frac{1}{E_{2,P}} - \frac{1}{2\omega}\right) |\langle P_2 | H_{DDI} | G \rangle|^2$$

where P_2 represents the bright polariton states in M_2 that have energies $E_{2,P}$ which differ from the uncoupled molecular energy, 2ω . By virtue of the completeness relationship, $\sum_{\lambda} |M_{2,\lambda}\rangle \langle M_{2,\lambda}| = \hat{I}$, the first term in Eq. (2) reduces to

$$E_{VDW} = -\sum_{\lambda} \frac{|\langle M_{2,\lambda} | H_{DDI} | G \rangle|^2}{2\omega} = -\frac{1}{2\omega} \sum_{i>j} T_{ij}^2$$
(2)

which recovers the standard vdW attraction and is isotropic (see Fig. 1a). The cavity-induced effect arises from the second term in Eq. (2), i.e., the contribution of the (bright) polariton manifold, P_2 , which consists of two sets of states, $P_{2,\pm}$ and $P_{2,\pm}^{\mu}$ (see the SI). First, the contribution to the energy shift coming from the polariton states $P_{2,\pm}$ is

$$-\Delta E_P^{(1)} = \sum_{\pm} \left(\frac{1}{E_{2,\pm}} - \frac{1}{2\omega} \right) \left| \langle P_{2,\pm} | H_{DDI} | G \rangle \right|^2 = \frac{\Omega_{4N-2}^2}{\omega (4\omega^2 - \Omega_{4N-2}^2)} \frac{1}{N(2N-1)} \left| \sum_{i>j} T_{ij} \right|^2 \quad (3)$$

where $\Omega_{4N-2} = \sqrt{4N-2}g$ is the effective Rabi frequency. Next, the contribution from $P_{2,\pm}^{\mu}$ is

$$-\Delta E_P^{(2)} = \sum_{\mu,\pm} \left(\frac{1}{E_{2,\pm}^{\mu}} - \frac{1}{2\omega} \right) \left| \left\langle P_{2,\pm}^{\mu} | H_{DDI} | G \right\rangle \right|^2 = \frac{\Omega_{N-2}^2}{\omega (4\omega^2 - \Omega_{N-2}^2)} \frac{1}{2(N-2)} \sum_{i,j,k} T_{ij} T_{jk} \tag{4}$$

where $\Omega_{N-2} = \sqrt{N-2}g$ is the effective Rabi frequency.

As illustrated in Fig. 1d and Fig. 1c, Eqs. (3) and (4) represent the cavity-induced 4-body and 3-body vdW interactions, respectively, and demonstrate the quantum nature of light-matter hybridization: (i) Without collective coupling to the cavity, these many-body terms cannot appear in the second-order perturbation, but require higher order treatment.²⁷ (ii) The pre-factors of these cavity-indued terms take the form

$$\text{prefactor} = \frac{\Omega_N^2}{\omega^2 - c\Omega_N^2} \tag{5}$$

which is renormalized by the effective Rabi frequency and is thus non-addictive in the molecular density. (iii) Since the predicted effect depends on the ratio Ω_N/ω , lower frequencies under vibrational strong coupling (VSC) can lead to larger enhancement than the coupling to electronic transitions. (iv) As discussed in the SI, the magnitudes of these contributions depend on the structure of the sample and scale differently with the molecular density in the gas, liquid, and solid phases.

Counter-rotating-wave term (CRW) The TCM is the RWA to the Dicke model^{21,28}, and the difference between the two models is the CRW term, $H_{CRW} = g(a^+\Sigma^+ + a\Sigma^-)$. The first contribution is

$$-E_{CRW}^{(1)} = \sum_{\pm} \frac{|\langle P_{2,\pm} | H_{CRW} | G \rangle|^2}{E_{2,\pm}} = \frac{2\omega \Omega_N^2}{(2\omega)^2 - \Omega_{4N-2}^2}$$
(6)

which introduces a one-body energy shift and can potentially lead to an orientational distribution with respect to the polarization direction of the cavity field. The second contribution arises from the cross term between H_{CRW} and H_{DDI} and is given explicitly as

$$-E_{CRW}^{(2)} = 2\sum_{\pm} \frac{\langle G|H_{CRW}|P_{\pm}\rangle\langle P_{\pm}|H_{DDI}|G\rangle}{E_{2,\pm}} = \frac{4g^2}{(2\omega)^2 - \Omega_{4N-2}^2} \sum_{i>j} T_{ij}$$
(7)

This term is pairwise with a non-additive pre-factor and a distance scaling of $1/R^3$, which results from the interaction of two dipoles induced by the cavity field (see Fig. 1b).

Dipole self-energy (DSE) The PF Hamiltonian also contains the dipole self-energy term in the form of $H_{DSE} = \Sigma^2 g^2 / \omega_c$, where $\Sigma = \sum_i (\sigma_i^- + \sigma_i^+)$ is the collective transition dipole. First-order



FIG. 1: Illustration of the various contributions to the vdW interaction in an optical cavity: (a) the standard isotropic and pairwise vdW interaction; (b) the pairwise interaction between cavity-induced dipoles with a distance scaling of $1/R^3$; (c) the 3-body contribution; (d) the 4-body contribution. Both the 3-body and 4-body terms arise from the cavity-induced quantum interference in dipole fluctuations.

perturbation evaluation of H_{DSE} yields the same form as in $E^{(1)}$ in Eq. (6) but with opposite sign. As a result, the two single-particle energy shifts due to H_{DSE} and H_{CRW} cancel exactly in the far off-resonance regime of $\omega_c \ll \omega_m$ and cancel by half at resonance $\omega_c = \omega_m$. The second contribution arises from the cross term between H_{DSE} and H_{DDI} and is identical to Eq. (7), i.e., the second contribution of the CRW Hamiltonian. A detailed derivation can be found in the SI.

Cavity frequency dependence The standard vdW attraction is a non-resonant effect, which is independent of the cavity frequency, as evidented in Eq. (2). In comparison, the cavity-induced corrections depend on the cavity frequency, introducing an additional control parameter. The above calculations are limited to the resonance case of $\omega_m = \omega_c = \omega$, which will now be generalized to the off-resonance case of $\omega_m \neq \omega_c$. For simplicity, we focus on the P_2^{μ} contribution to the energy shift,



FIG. 2: Illustration of various structural orders in condensed phase vdW systems: (a) intermolecular orientational order of spherical particles; (b) orientational order of non-spherical particles; (c) collective attraction between a cavity vdW system and an external slab.

$$\Delta E_P^{(2)}, \text{ which dominates the the many-body interference effect. Then, Eq. (4) is generalized to} -\Delta E_P^{(2)} = \sum_{\mu,\pm} \left(\frac{1}{E_{2,\pm}^{\mu}} - \frac{1}{2\omega_m} \right) \left| \left\langle P_{2,\pm}^{\mu} | H_{DDI} | G \right\rangle \right|^2 = \left[\frac{2\omega_m}{(2\omega_m + \delta)^2 - \Delta_{N-2}^2} - \frac{1}{2\omega_m} \right] \sum_{\mu} |\langle s_2^{\mu} | H_{DDI} | g \rangle|^2$$

where the frequency detuning is $\delta = (\omega_c - \omega_m)/2$, $\Omega_{N-2} = \sqrt{N-2}g$, and $\Delta_{N-2} = \sqrt{\Omega_{N-2}^2 + \delta^2}$. In comparison with the resonant result in Eq. (4), positive detuning reduces the pre-factor and thus suppresses the interference effect, whereas negative detuning does the opposite and enhances the interference effect. As we further increase the cavity frequency such that $\delta > \delta_c$, with the crossover detuning $\delta_c = \frac{\Omega_{N-2}^2}{4\omega_m}$, then $\Delta E_P^{(2)} \ge 0$. As a result, the cavity-induced non-additive interaction can reduce the vdW attraction or even change attraction to repulsion. This prediction is consistent with the dramatic effects of frequency detuning reported in a recent *ab initio* simulation.⁹

Orientational order The scalar formulation presented thus far should be understood as a projec-

tion into the polarization of the cavity field and can predict structural changes in cavity systems. Specifically, the LM interaction and resulting hybrid states are all defined in the polarization direction of the cavity field (i.e., the z axis): The transition dipole is the projection along the polarization, μ_z , the dipole-dipole interaction is the z-projection of the dipole tensor \mathcal{T} , $T = \mu_z \mathcal{T}_{zz} \mu_z$, and the coupling strength to the cavity field is also defined similarly as $g = \mu_z g_0/\mu$ where g_0 is the maximal coupling constant, and $\mu = |\vec{\mu}|$ is the magnitude of the transition dipole. In the perpendicular directions, the molecular states are unperturbed. As a result, the leading order in the vdW attraction in Eq. (2) recovers the isotropic vdW potential, whereas the cavity-induced modifications are along the polarization direction of the cavity field and thus break the isotropic distribution of the cavity-free molecular sample. Consider the following different cases:

- 1. Spherical particles have no orientational preferences, so the orientational order exists not on individual particles but between particles. The cavity-induced many-body polarization effects align the intermolecular axis and can potentially lead to an orientational order, similar to the smectic phase in liquid crystals (see Fig. 2a).
- 2. An interesting scenario arises when the spherical symmetry of individual particles is broken, as in most molecules. The principal molecular axis indicates the preferential polarizability direction, and the transition dipole is defined in the molecular frame as $\vec{\mu}_i(\hat{\Omega}_i)$, where $\hat{\Omega}_i$ is the solid angle associated with the i-th molecule.²⁹ As a result, the cavity field can align both the molecular axis on the single-particle level and the intermolecular axis on the ensemble level, creating both the nematic and smectic orders (see Fig. 2b).^{8,30,31}
- 3. In addition to induced dipoles, most molecules possess permanent dipoles, which will reinforce both the dipole-dipole interaction and the light-matter interaction. The permanent dipoles in polarizable systems have been studied within the Drude oscillator model and show a prominent effect in the dielectric constant and dielectric response.³² The light-matter interaction in polarizable dipolar systems is an interesting topic for future study.

vdW interaction with external objects In addition to the homogenous polarizable system considered so far, another interesting scenario is the vdW interaction with an external object, such as a mirror in the Fabry-Perot (FP) cavity or a surface in a plasmonic cavity. The presence of such an external object breaks the spatial homogeneity and naturally reinforces the interference effect in the vdW interaction. As an illustrative example, we consider the coupling between a 2D molecular thin film and a molecular sample in the cavity separated by a distance z_0 , as illustrated in Fig. 2c. Assuming that the spatial extension of the thin film is much larger than z_0 , we integrate over the area of the thin film and obtain the scaling relationships,

$$-E_{vdW} \propto \sum_{i} |T_{0i}|^2 = \int \int dx dy \frac{\rho_2}{(x^2 + y^2 + z_0^2)^3} \propto \frac{\rho_2}{z_0^4}$$
$$-E_{vdW}^{cav} \propto |\sum_{i} T_{0i}|^2 = \left[\int dx \int dy \frac{\rho_2}{(x^2 + y^2 + z_0^2)^{3/2}}\right]^2 \propto \frac{\rho_2^2}{z_0^2}$$

where ρ_2 is the molecular density of the 2D plane. As suggested by the different scalings with respect to z_0 , the cavity-induced vdW interaction has a much longer interaction range than the standard vdW attraction. This effect is related to the cavity Casimir-Polder forces and generally depends on the shape and dimension of the external object.^{13,33,34}

Further, we comment on the potential role of the enhanced attraction to the cavity surface in cavity-catalyzed reactions. With the enhanced range and strength, the cavity wall or mirror can attract reactive molecules in an optical cavity and thus create a high density molecular layer. The surface-bound molecule can potentially modify its structure and thus change its reactivity. As suggested in Eq. (5), the cavity effect scales generally as Ω^2/ω^2 and is thus stronger for the vibrational coupling than for the electronic coupling, so the surface effect can be relevant in the vibrational strong-coupling (VSC) regime.^{13,14,19}

Conclusion In summary, with a second-order perturbation on the hybrid light-mater state basis, we predicted the coorperativity and interference of vdW interactions in optical cavities: (i) In addition to the standard pairwise interaction, the dipole fluctuations in cavities lead to 3-body and 4body vdW interactions, which increase with molecular density and can align intermolecular vectors. (ii) Both the DSE and CRW terms contribute constant energy shifts on the single-particle level and pairwise interactions between cavity-induced dipoles. Depending on the relative orientation, the latter interaction can be repulsive or attractive and scales with the distance as R^{-3} . (iii) The prefactors of these cavity-induced interactions depend on the cavity frequency and scale with molecular density and light-matter coupling nonlinearly. (iv) For the interaction with an external object, such as a wall or mirror, the interference effect leads to distinct distance scaling laws and significantly enhances the interaction range and strength. These predictions suggest the possibility of structural changes, in particular, the emergence of nematic or smectic order, and may help explain recent cavity experiments. We now commend briefly on the relevance of the cavity-induced effects in realistic systems: (i) The leading-order coefficient of the many-body terms in Eqs. (4) and (3) scales with the ratio of Ω_N^2/ω_m^2 , which can reach the range of 0.1 in the strong coupling regime. (ii) The collectivity in the LM interaction leads to non-linear N-scaling in Eq. (5), which has been observed in simulations.^{9,10} (iii) The R^{-3} term in Eqs. (7) has been analyzed on the pairwise level^{10,12} and can be further enhanced by the collective correction.

Though the current analysis is devoted to the vdW interaction in optical cavities, the basic idea that optical cavities can modulate intermolecular potentials collectively is general and can be applied to other types of interactions including hydrogen bonding. As a result, the unusual dynamical properties in cavities can arise not only from the dynamical response due to the light-matter hybridization, but also from the structural modifications due to the cavity-induced intermolecular interactions. Further theoretical study can extend the current analysis from a single-photon mode to a multi-mode cavity,³⁵ which leads to the longitudinal component and retardation in the dipolar coupling; however, the interference and collective effects predicted here are expected to remain effective. Another direction to explore is the cavity-modified interactions under VSC, which may help understand the intriguing discovery of cavity-catalyzed chemical reactions.

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