

Polaritonic States of Matter in a Rotating Cavity

Lorenz S. Cederbaum*



Cite This: *J. Phys. Chem. Lett.* 2021, 12, 6056–6061



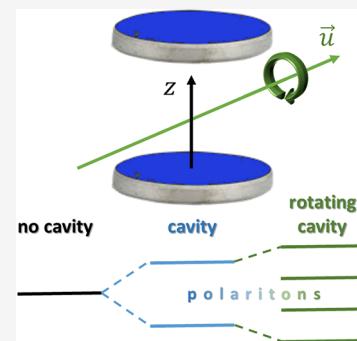
Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: The interaction of quantum light with matter like that inside a cavity is known to give rise to mixed light–matter states called polaritons. We discuss the impact of rotation of the cavity on the polaritons. It is shown that the number of polaritons increases because of this rotation. The structure of the original polaritons is modified, and new ones are induced by the rotation that strongly depend on the angular velocity and the choice of axis of rotation. In molecules the rotation can change the number of light-induced conical intersections and their dimensionality and hence strongly impact their quantum dynamics. General consequences are discussed.



The coupling of matter excitations with a quantized radiation field like that inside a cavity has become an extensive field of research. This coupling leads to the formation of hybrid light–matter states called polaritons or polaritonic states and opens up many possibilities to enhance or suppress available mechanisms, to mediate new ones, and to manipulate and control the properties of the matter. The list of work published in this field has grown immensely. Here, we just mention as examples the possibilities to control chemical reactions by varying the quantized field,^{1–4} to control photochemical reactivity,^{5,6} to enhance energy transfer^{7,8} and charge transfer,^{7,9–11} as well as to induce molecular non-adiabatic processes.^{3,12–17}

We study the impact of rotation of a cavity on the polaritons of atoms and molecules interacting resonantly with the cavity and show that the effects induced by the rotation can be rather severe. Because it is the first work on the subject, we concentrate here on the fundamental aspect of this impact and do not discuss technical details of the cavity and possible back-actions of the rotation on the cavity. The physics of rotating systems has attracted much attention in many contexts. For instance, ultracold bosonic gases under rotation probe phenomena of quantum systems, including quantized vortices,^{18,19} enhancement of many-body effects in the excitation spectrum,²⁰ and much more. Extensive literature on rotating Bose–Einstein condensates is found in reviews.^{21,22} Other subjects of interest in rotating systems comprise geometric quantum phases,^{23,24} quantum rings,^{25,26} electroweak interactions,²⁷ spintronics,^{28,29} and induced electric dipole moment interacting with external fields.³⁰

We consider an ensemble of N noninteracting identical atoms or molecules in a cavity with a quantized light mode (cavity mode) of frequency ω_c and polarization direction \vec{e}_c

and let the cavity rotate with a uniform angular velocity Ω around an axis u . The total Hamiltonian H_L of the ensemble plus rotating cavity and the solution of the time-dependent Schrödinger equation Ψ_L in the laboratory frame can be expressed by the respective quantities in the rotating frame (RF) by employing the rotation operator $\hat{O}_u = \exp(-i\Omega\vec{u}\cdot\vec{L}t/\hbar)$, where \vec{u} is the unit vector along the rotation axis and \vec{L} is the total angular momentum of all particles. Inserting $H_L = \hat{O}_u H_{\text{RF}} \hat{O}_u^\dagger$ and $\Psi_L = \hat{O}_u \Psi_{\text{RF}}$ into the Schrödinger equation in the laboratory frame, one readily finds

$$i\hbar \frac{\partial \Psi_{\text{RF}}}{\partial t} = [H_{\text{RF}} - \vec{\Omega} \cdot \vec{L}] \Psi_{\text{RF}} \quad (1)$$

for the Schrödinger equation in the rotating frame, where $\vec{\Omega} = \Omega\vec{u}$. In this frame, the Hamiltonian H_{RF} is time-independent, is just the total Hamiltonian of the ensemble–cavity system with a nonrotating cavity, and reads^{31–33}

$$H_{\text{RF}} = H_e + \hbar\omega_c \hat{a}^\dagger \hat{a} + g_0 \vec{e}_c \cdot \vec{d} (\hat{a}^\dagger + \hat{a}) \quad (2)$$

where $H_e = \sum_{i=1}^N H_i$ is the Hamiltonian of the ensemble, $\vec{d} = \sum_{i=1}^N \vec{d}_i$ the total dipole operator of the ensemble, and g_0 the coupling strength between the cavity and the atoms. The

Received: May 17, 2021

Accepted: June 22, 2021

quadratic dipole self-energy term is neglected as it is of relevance only for very strong coupling.

We start with a single atom and assume its excitation energy to be resonant with the cavity mode. For simplicity of presentation, we choose the angular momentum of the atom in its ground state $\phi_{l,m}$ to be $l = 0$ and $l = 1$ in its excited state $\psi_{l,m}$ and take the ground-state energy to be the zero of the energy scale. As usual, we resort to the single-excitation space where the contributing states are the atom in its ground state and the cavity in a single photon state denoted by $\phi_{0,0}1_c$ and the atom in its excited state with the cavity having zero photons denoted analogously. Without rotation, the Hamiltonian of the atom–cavity system is known to have two solutions $\Phi_{\text{up/lp}} = (\phi_{0,0}1_c \pm \psi_{1,0}0_c)/\sqrt{2}$ with energies $E_{\text{up/lp}} = \hbar\omega_c \pm g$ called upper and lower polaritons, where $g = g_0 d_z$ and d_z is the z component of the transition dipole. Owing to the dipole interaction, only the $m = 0$ state of the excited states contributes.

The situation changes once the cavity rotates. We emphasize that the rotation refers to the polarization direction of the cavity and not necessarily to the physical rotation of the cavity components. The angular momentum operator of the center of mass of the atom contributes the same to all states and can be ignored, and one is left in eq 1 with the electronic angular momentum operator \vec{L} . In general, all three excited states $\psi_{1,m}$, $m = 0, \pm 1$ of the atom must be considered now. Only if the rotation axis u coincides with the polarization direction of the cavity, the $m = \pm 1$ states decouple and can be ignored. Next we call the polarization direction z and rotate the cavity in the xy -plane. In the space spanned by $\phi_{0,0}1_c$ and the three $\psi_{1,m}0_c$ states, the Hamiltonian $\mathcal{H} = [H_{\text{RF}} - \vec{\Omega} \cdot \vec{L}]$ is represented by the matrix

$$\mathcal{H} = \begin{pmatrix} \hbar\omega_c & g & 0 & 0 \\ g & \hbar\omega_c & -\hbar\Omega_- & -\hbar\Omega_+ \\ 0 & -\hbar\Omega_+ & \hbar\omega_c & 0 \\ 0 & -\hbar\Omega_- & 0 & \hbar\omega_c \end{pmatrix} \quad (3)$$

where the ladder operators $L_{\pm} = (L_x \pm iL_y)/\sqrt{2}$ and $\Omega_x L_x + \Omega_y L_y = \Omega_+ L_+ + \Omega_- L_-$ are introduced. The matrix is Hermitian as $\Omega_-^\dagger = \Omega_+$. We see that the cavity mode couples directly only to the $m = 0$ excited state, but this state couples to the $m = \pm 1$ states.

To proceed, we diagonalize the lower right 3×3 block of the above matrix, and the resulting eigenvectors can be used as a basis for the excited electronic manifold in which the Hamiltonian \mathcal{H} becomes an arrowhead matrix,^{34–36} which is particularly helpful when extending the problem to N atoms. The new basis can be given explicitly. The state $\psi_0 = (\Omega_+\psi_{1,1}0_c - \Omega_-\psi_{1,-1}0_c)/\Omega$ has the energy $\hbar\omega_c$ and decouples from all the other states including the cavity one photon state $\phi_{0,0}1_c$ and hence can be addressed as a dark state. Notice that this state is entangled because of rotation of the cavity. The remaining states read $\psi_{\pm} = [\psi_{1,0}0_c \mp (\Omega_+\psi_{1,1}0_c + \Omega_-\psi_{1,-1}0_c)/\Omega]/\sqrt{2}$. Without the dark state, the matrix Hamiltonian in the $\phi_{0,0}1_c$ and ψ_{\pm} basis now takes on the simple appearance

$$\mathcal{H} = \begin{pmatrix} \hbar\omega_c & g/\sqrt{2} & g/\sqrt{2} \\ g/\sqrt{2} & \hbar(\omega_c + \Omega) & 0 \\ g/\sqrt{2} & 0 & \hbar(\omega_c - \Omega) \end{pmatrix} \quad (4)$$

where Ω is the angular velocity of the cavity. The eigenvalues and eigenvectors are easily obtained. Interestingly, one of the eigenvalues is again just $\hbar\omega_c$, but in contrast to the above-mentioned state, this state is not a dark state. Apart from a normalization constant, it reads $[(\hbar\Omega\sqrt{2}/g)\phi_{0,0}1_c + \psi_- - \psi_+]$; that is, this state is a new kind of a polariton and is induced solely by the rotation of the cavity. Although modified by the rotation, the other two states are reminiscent of the upper and lower polaritons present in the nonrotating cavity. Their energies are also modified by the rotation giving $E_{\text{up/lp}} = \hbar\omega_c \pm [\hbar^2\Omega^2 + g^2]^{1/2}$.

What happens when more atoms are present in the cavity? For N atoms without rotation it is well-known that there are two polaritons with energy $E_{\text{up/lp}}(N) = \hbar\omega_c \pm \sqrt{N}g$ and $N - 1$ dark states at $\hbar\omega_c$. For a rotating cavity there are $3N + 1$ states playing a role as each atom contributes 3 excited states. As we have seen above, for each atom one dark state entangled by the rotation can be decoupled. To investigate the remaining $2N + 1$ states, one can extend the matrix Hamiltonian in eq 4 by repeating N times the lower right 2×2 block along the diagonal and extending the first row and column by $g/\sqrt{2}$ coupling elements. The resulting arrowhead matrix can be solved,^{34–36} and the polaritons follow from the Dyson-like equation $E - \hbar\omega_c = g^2 N/2[1/[E - \hbar(\omega_c + \Omega)] + 1/[E - \hbar(\omega_c - \Omega)]]$, which readily leads to the eigenenergies

$$\begin{aligned} E_{\text{up/lp}} &= \hbar\omega_c \pm [(\hbar\Omega)^2 + Ng^2]^{1/2} \\ E_0 &= \hbar\omega_c \end{aligned} \quad (5)$$

As found for a single atom, there are three polaritons: two of them reminiscent of those in a nonrotating cavity and one at $\hbar\omega_c$ induced by the rotation. In addition, there are $N - 1$ dark states at energy $\hbar(\omega_c + \Omega)$ and $N - 1$ dark states at energy $\hbar(\omega_c - \Omega)$. That is, this kind of dark state is doubled and shifted by the rotational frequency compared to the case of a nonrotating cavity.

Above, we have seen that there is no impact of rotation for a cavity rotating around its polarization direction and that the impact is severe when the rotation axis is perpendicular to the polarization direction. What if the unit vector \vec{u} along the rotation axis has components in all directions? Then, indeed, also Ω_z contributes and makes the outcome even more intricate. We first return to a single atom and to the Hamiltonian matrix in eq 3. The action of $-\hbar\Omega_z$ has to be added to this matrix. That is, $-\hbar\Omega_z$ has to be added to the third element along the diagonal and $\hbar\Omega_z$ to the last one. Now, one can proceed and diagonalize the lower right 3×3 block of the matrix and use the resulting eigenvectors as a new basis to represent the Hamiltonian. The resulting Hamiltonian matrix takes on the following appearance:

$$\mathcal{H} = \begin{pmatrix} \hbar\omega_c & \tilde{g}\Omega_{xy}/\Omega & \tilde{g}\Omega_{xy}/\Omega & g\Omega_z/\Omega \\ \tilde{g}\Omega_{xy}/\Omega & \hbar(\omega_c + \Omega) & 0 & 0 \\ \tilde{g}\Omega_{xy}/\Omega & 0 & \hbar(\omega_c - \Omega) & 0 \\ g\Omega_z/\Omega & 0 & 0 & \hbar\omega_c \end{pmatrix} \quad (6)$$

where $\tilde{g} = g/\sqrt{2}$ and $\Omega_{xy} = (\Omega_x^2 + \Omega_y^2)^{1/2}$ is the effective angular velocity in the xy -plane. Note that $\Omega^2 = \Omega_{xy}^2 + \Omega_z^2$. By putting Ω_z to zero, one of the states decouples and becomes a dark state of energy $\hbar\omega_c$ and one immediately recovers the Hamiltonian in eq 4 for the polaritons in the cavity rotating around an axis in the xy -plane.

A major outcome of the above discussion is that if the axis of rotation is neither parallel to the polarization axis nor in the plane perpendicular to it, one obtains four polaritons instead of two in the nonrotating cavity. Two of the polaritons are induced solely by the rotation.

If we have N atoms in the rotating cavity, the Hamiltonian can be obtained from that in eq 6 by repeating N times the lower right 3×3 block along the diagonal and extending the first row and column by N times the coupling trio $\tilde{g}\Omega_{xy}/\Omega$, $\tilde{g}\Omega_{xy}/\Omega$, $g\Omega_z/\Omega$. Again, the resulting arrowhead matrix can be solved and the polaritonic states follow from the Dyson-like equation $E - \hbar\omega_c = (\tilde{g}\Omega_{xy}/\Omega)^2 N [1/[E - \hbar(\omega_c + \Omega)] + 1/[E - \hbar(\omega_c - \Omega)]] + (g\Omega_z/\Omega)^2 N/[E - \hbar\omega_c]$ which can be solved explicitly giving the four energies of the polaritons:

$$E_{\text{polariton}} = \hbar\omega_c \pm \frac{1}{\sqrt{2}} \{[(\hbar\Omega)^2 + Ng^2] \pm \{[\hbar^2(\Omega_{xy}^2 - \Omega_z^2) + Ng^2]^2 + 4\hbar^4\Omega_{xy}^2\Omega_z^2\}^{1/2}\}^{1/2} \quad (7)$$

The different impact of Ω_z and Ω_{xy} is clearly seen in the above polaritonic energies. The four polariton branches are accompanied by $3N - 3$ dark states, $N - 1$ at energy $\hbar\omega_c$ and $N - 1$ at each of the energies $\hbar(\omega_c \pm \Omega)$. The setup and the resulting polaritons are schematically shown in Figure 1.

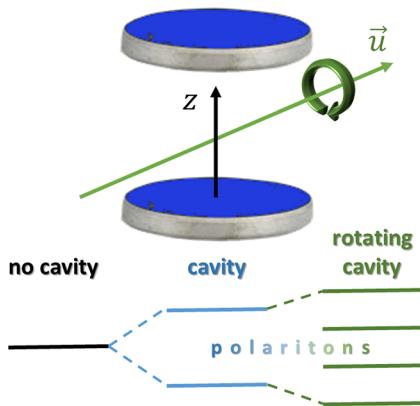


Figure 1. Schematic picture of the rotating cavity and the resulting polaritons. Without rotation there are two polaritons, the so-called upper and lower polaritons. The polarization direction of the cavity is along the z axis. The cavity rotates with a uniform angular velocity, and \vec{u} is the unit vector along the rotation axis. In the general case shown in the figure, there are four polaritons. Special cases where \vec{u} is parallel or perpendicular to z are discussed in the text.

We now turn to molecules. Because of the additional vibrational and rotational degrees of freedom, the treatment of molecules is more involved. A particularly intriguing quantity in polyatomic molecules are conical intersections (CIs) which lead to singular coupling between the electronic and nuclear degrees of freedom.^{37,38} Classical laser fields can induce new CIs, named light-induced CIs (LICIs), even in a single diatomic molecule.^{39–41} A quantized radiation field also induces LICIs in a diatomic molecule with new implications for their dynamic properties^{14,15,42} and, of course, also in polyatomic molecules.^{15,16} New types of intersections appear when more molecules interact via the quantized field, like collective CIs which lead to unusual dynamics.¹⁷

Each type of molecule has to be treated by itself, as its structure and the nature of its electronic ground and excited states play a role. To be specific we consider a closed-shell homonuclear diatomic molecule in a cavity where its ground state with one cavity photon $\phi_\Sigma 1_c$ interacts with a doubly degenerate $\psi_{\Pi} 0_c$ state of Π symmetry with zero photons. This example has the ingredients needed for understanding how to treat other systems. We proceed in three steps. First, we freeze the nuclear motion of the molecule and consider the electronic–cavity Hamiltonian for the system in a nonrotating cavity; that is, the internuclear distance r and the rotational angles θ and φ are kept fixed and have the role of parameters. In the space of the above states this Hamiltonian is a 3×3 matrix, but one can transform the components of the degenerate $\psi_{\Pi} 0_c$ state such that one component decouples, resulting effectively in a 2×2 matrix (see, for example, ref 43). In a rotating cavity the Hamiltonian cannot be reduced and stays a 3×3 matrix.

Choosing $\psi_{\Pi_\pm} = (\psi_{\Pi_x} \pm \psi_{\Pi_y})/\sqrt{2}$, one obtains the following electronic–cavity Hamiltonian for the system in a nonrotating cavity:

$$\begin{pmatrix} V_\Sigma(r) + \hbar\omega_c & g(r)\sin(\theta)/\sqrt{2} & g(r)\sin(\theta)/\sqrt{2} \\ g(r)\sin(\theta)/\sqrt{2} & V_\Pi(r) & 0 \\ g(r)\sin(\theta)/\sqrt{2} & 0 & V_\Pi(r) \end{pmatrix} \quad (8)$$

V_Σ and V_Π are the potential energies corresponding to the ϕ_Σ and ψ_Π electronic states, $g(r) = g_0 d_{\Sigma\Pi}(r)$, where $d_{\Sigma\Pi}$ is the transition dipole moment between the two electronic states ϕ_Σ and ψ_{Π_x} and depends on the interatomic distance; $d_{\Sigma\Pi}\sin(\theta)$, where θ is the angle between the molecular axis and the cavity polarization, is the projection of the moment on the polarization direction. It is easily seen that a rotation of the degenerate Π -states by $\pi/4$ leads to the decoupling of one of them.

In the second step we allow the cavity to rotate and consider the impact of adding $-\vec{\Omega} \cdot \vec{L}$ to the electronic–cavity Hamiltonian in eq 8. We denote the resulting matrix Hamiltonian by \mathcal{H}_{ec} to distinguish it from that of the total Hamiltonian \mathcal{H} which includes the nuclear motion of the molecule. To bring a diatomic molecule into a general position in the cavity, we start with the molecule along the z -axis and rotate it first by an angle θ around the y -axis and then by an angle φ around the z -axis. The resulting rotation matrix \mathbf{R} is

$$\mathbf{R} = \begin{pmatrix} \cos(\varphi)\cos(\theta) & -\sin(\varphi) & -\cos(\varphi)\sin(\theta) \\ \sin(\varphi)\cos(\theta) & \cos(\varphi) & -\sin(\varphi)\sin(\theta) \\ \sin(\theta) & 0 & \cos(\theta) \end{pmatrix} \quad (9)$$

The states $\psi_{\Pi_{\pm}}$ are transformed by the rotation to become $U(\mathbf{R})\psi_{\Pi_{\pm}}(\vec{r}_e) = \psi_{\Pi_{\pm}}(\mathbf{R}^{-1}\vec{r}_e)$, where \vec{r}_e indicates the electronic coordinates. To determine the matrix elements of the electronic angular momentum between the rotated states, we use the fact that the angular momentum is a vector and hence⁴⁴

$$\mathcal{H}_{ec} = \begin{pmatrix} V_{\Sigma}(r) + \hbar\omega_c & g(r)\sin(\theta)/\sqrt{2} & g(r)\sin(\theta)/\sqrt{2} \\ g(r)\sin(\theta)/\sqrt{2} & V_{\Pi}(r) - f(\varphi)\sin(\theta) + \cos(\theta)\hbar\Omega_z & 0 \\ g(r)\sin(\theta)/\sqrt{2} & 0 & V_{\Pi}(r) + f(\varphi)\sin(\theta) - \cos(\theta)\hbar\Omega_z \end{pmatrix} \quad (11)$$

where $f(\varphi) = \hbar(\Omega_+e^{i\varphi} + \Omega_-e^{-i\varphi})/\sqrt{2}$ is a real function of φ . Two consequences are immediately seen: Even if the rotation is only around the polarization axis, three polaritons emerge, and for a general rotation, the azimuthal angle enters and the polaritons now depend on the three parameters r , θ , and φ .

As seen from eq 8, two LICIs between the potential energy surfaces (eigenvalues) of the Hamiltonian appear in a nonrotating cavity for $\theta = 0, \pi$ at the value of r where the condition $V_{\Sigma}(r) + \hbar\omega_c = V_{\Pi}(r)$ is met.⁴³ If the cavity rotates around z , the number of LICIs doubles. The condition $\theta = 0, \pi$ still applies for all LICIs. One pair of LICIs appears at r_+ and one at r_- where $V_{\Sigma}(r_{\pm}) + \hbar\omega_c = V_{\Pi}(r_{\pm}) \pm \hbar\Omega_z$ is fulfilled, respectively. If the cavity rotates around a general axis, the potential surfaces become three-dimensional as they also depend on the angle φ . In three dimensions, CIs are not anymore distinct points but one-dimensional hypersurfaces in nuclear coordinate space.^{37,38} Indeed, for a rotating cavity around a general axis, the conditions for a LICI are the same as above and each of the four LICIs exists on a seam $2\pi \geq \varphi \geq 0$. As LICIs have substantial effect on the dynamics of molecules, the present result shows that one can investigate the impact of a seam of LICI for a diatomic molecule by rotating the cavity.

In the third step we take into account the vibrational and rotational motions and consider the total Hamiltonian $\mathcal{H} = H_{RF} - \vec{\Omega} \cdot \vec{\mathcal{L}}$ including the respective kinetic energies and also the common rotational angular momentum $\vec{L}_{\varphi\theta}$ of the molecule in $\vec{\mathcal{L}} = \vec{L} + \vec{L}_{\varphi\theta}$. The kinetic energy operator of a diatomic molecule is $-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + \frac{L_{\varphi\theta}^2}{2\mu r^2}$, where μ is the reduced mass of the molecule. Adding to it the impact $-\vec{\Omega} \cdot \vec{L}_{\varphi\theta}$ of the rotation of the cavity gives rise to the final Hamiltonian of the molecule interacting with the rotating cavity

$$\mathcal{H} = \left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + \frac{(\vec{L}_{\varphi\theta} - \mu r^2 \vec{\Omega})^2}{2\mu r^2} - \frac{\mu r^2 \Omega^2}{2} \right] \mathbf{1} + \mathcal{H}_{ec} \quad (12)$$

where $\mathbf{1}$ is a unity 3×3 matrix and \mathcal{H}_{ec} is the electronic-cavity Hamiltonian in eq 11. All the coordinates r , θ , and φ are now dynamic variables. The rotation of the cavity not only influences severely the structure of the polaritons as discussed

$$\langle \psi_{\Pi_{\pm}} | U^\dagger(\mathbf{R}) \vec{L} U(\mathbf{R}) | \psi_{\Pi_{\pm}} \rangle = \langle \psi_{\Pi_{\pm}} | \mathbf{R} \vec{L} | \psi_{\Pi_{\pm}} \rangle \quad (10)$$

This implies that the matrix element of each component of the angular momentum vector between any two rotated states can be expressed as a linear combination of the matrix elements of all the components between the respective unrotated states. The latter are usually known.

In the present case of a diatomic molecule only the diagonal matrix elements of L_z do not vanish, and as the $\psi_{\Pi_{\pm}}$ are eigenstates of L_z , $L_z \psi_{\Pi_{\pm}} = \pm \psi_{\Pi_{\pm}}$, the resulting electronic-cavity Hamiltonian \mathcal{H}_{ec} takes on the following appearance:

$$\begin{pmatrix} V_{\Sigma}(r) + \hbar\omega_c & g(r)\sin(\theta)/\sqrt{2} & g(r)\sin(\theta)/\sqrt{2} \\ g(r)\sin(\theta)/\sqrt{2} & V_{\Pi}(r) - f(\varphi)\sin(\theta) + \cos(\theta)\hbar\Omega_z & 0 \\ g(r)\sin(\theta)/\sqrt{2} & 0 & V_{\Pi}(r) + f(\varphi)\sin(\theta) - \cos(\theta)\hbar\Omega_z \end{pmatrix} \quad (11)$$

above; the rotation and vibration of the molecules are affected as well.

The rotation of a cavity changes the number of the polaritons found without rotation. Their number increases because of this rotation. The rotation modifies the structure of the original polaritons and induces new ones which strongly depend on the angular velocity and the choice of axis of rotation with respect to the polarization of the cavity mode. In molecules the rotation can change the number of LICIs and their dimensionality and hence impact the molecular dynamics. If the axis of rotation differs from the cavity polarization direction, a seam of LICIs appears even in a diatomic molecule. Changing the axis of rotation would allow the investigation of the quantum dynamics due to a LICI seam.

It has been shown (see, e.g., the discussion below eq 4) that $\hbar\Omega/g$ is the relevant parameter which can be used to estimate the impact of the rotation of the cavity. This parameter determines the energy shifts due to the rotation and more importantly the mixing of states, which gives rise to the appearance of additional polaritons. These polaritons appear at energies rather different from those without rotation. In the case of molecules, even relatively small $\hbar\Omega/g$ can lead to substantial dynamical effects due to changes induced in the LICIs by the rotation. We re-emphasize that the rotation refers to the polarization direction of the cavity and not necessarily to the physical rotation of the cavity components, and one may anticipate that fast rotations of the polarization direction might be achieved by optical means.

The impact of rotation on the polaritons of an ensemble of N noninteracting identical atoms has been investigated as well. The number of polaritonic branches is the same as for an individual atom, but the number of dark states increases compared to a nonrotating cavity by a factor of 2 or 3 depending on the axis of rotation, and interestingly, their energy is shifted by the rotation. The Hamiltonian matrix for a diatomic molecule can be straightforwardly extended to accommodate N noninteracting identical ones, similar to that done for the atoms. However, as discussed before,¹⁷ the matrix is an operator in the N -dimensional (in the present case $3N$ -dimensional) nuclear coordinate space as each molecule possesses its own dynamical variables, and this makes the analysis rather intricate and is left for the future.

The study can also be extended to polyatomic molecules. Here, one has to resort to three angles instead of the two for diatomics. In general, Euler angles are a good choice, and with them a strategy similar to that applied here for the diatomic molecules can be employed.^{44,45} Additional extensions of interest include the investigation of other atomic electronic angular momenta; of atoms and molecules with spin-orbit coupling; and as a long-term project, of an ensemble of interacting atoms or molecules.

■ AUTHOR INFORMATION

Corresponding Author

Lorenz S. Cederbaum — *Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, Heidelberg D-69120, Germany;* orcid.org/0000-0002-4598-0650; Email: Lorenz.Cederbaum@pci.uni-heidelberg.de

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.jpclett.1c01570>

Notes

The author declares no competing financial interest.

■ ACKNOWLEDGMENTS

The author thanks O. E. Alon and A. I. Kuleff for valuable contributions and A. Vibók for convincing him that cavities are interesting. Financial support by the European Research Council (ERC) (Advanced Investigator Grant No. 692657) is gratefully acknowledged.

■ REFERENCES

- (1) Ebbesen, T. W. Hybrid light-matter states in a molecular and material science perspective. *Acc. Chem. Res.* **2016**, *49*, 2403.
- (2) Kowalewski, M.; Mukamel, S. Manipulating molecules with quantum light. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114*, 3278–3280.
- (3) Feist, J.; Galego, J.; Garcia-Vidal, F. J. Polaritonic chemistry with organic molecules. *ACS Photonics* **2018**, *5*, 205–216.
- (4) Thomas, A.; Lethuillier-Karl, L.; Nagarajan, K.; Vergauwe, R.; George, J.; Chervy, T.; Shalabney, A.; Devaux, E.; Genet, C.; Moran, J.; Ebbesen, T. W. Tilting a ground state reactivity landscape by vibrational strong coupling. *Science* **2019**, *363*, 615–619.
- (5) Schwartz, T.; Hutchison, J. A.; Genet, C.; Ebbesen, T. W. Reversible switching of ultrastrong light-molecule coupling. *Phys. Rev. Lett.* **2011**, *106*, 196405.
- (6) Stranius, K.; Hertzog, M.; Börjesson, K. Selective manipulation of electronically excited states through strong light-matter interactions. *Nat. Commun.* **2018**, *9*, 2273.
- (7) Schäfer, C.; Ruggenthaler, M.; Rubio, A. Modification of excitation and charge transfer in cavity quantum electrodynamical chemistry. *Proc. Natl. Acad. Sci. U. S. A.* **2019**, *116*, 4883–4892.
- (8) Du, M.; Martinez-Martinez, L. A.; Ribeiro, R. F.; Hu, Z.; Menon, V. M.; Yuen-Zhou, J. Theory for polariton-assisted remote energy transfer. *Chem. Sci.* **2018**, *9*, 6659–6669.
- (9) Herrera, F.; Spano, F. C. Cavity-controlled chemistry in molecular ensembles. *Phys. Rev. Lett.* **2016**, *116*, 238301.
- (10) Semenov, A.; Nitzan, A. Electron transfer in confined electromagnetic fields. *J. Chem. Phys.* **2019**, *150*, 174122.
- (11) Mandal, A.; Krauss, T. D.; Huo, P. Polariton-mediated electron transfer via cavity quantum electrodynamics. *J. Phys. Chem. B* **2020**, *124*, 6321–6340.
- (12) Kowalewski, M.; Bennett, K.; Mukamel, S. Non-adiabatic dynamics of molecules in optical cavities. *J. Chem. Phys.* **2016**, *144*, 054309.
- (13) Bennett, K.; Kowalewski, M.; Mukamel, S. Novel photochemistry of molecular polaritons in optical cavities. *Faraday Discuss.* **2016**, *194*, 259–282.
- (14) Szidarovszky, T.; Halasz, G. J.; Csaszar, A. G.; Cederbaum, L. S.; Vibok, A. Conical intersections induced by quantum light: Field-dressed spectra from the weak to the ultrastrong coupling regimes. *J. Phys. Chem. Lett.* **2018**, *9*, 6215–6223.
- (15) Gu, B.; Mukamel, S. Manipulating nonadiabatic conical intersection dynamics by optical cavities. *Chem. Sci.* **2020**, *11*, 1290–1298.
- (16) Fabri, C.; Halasz, G. J.; Cederbaum, L. S.; Vibok, A. Born–Oppenheimer approximation in optical cavities: from success to breakdown. *Chem. Sci.* **2021**, *12*, 12511251–1258–1258.
- (17) Vendrell, O. Collective Jahn-Teller interactions through light-matter coupling in a cavity. *Phys. Rev. Lett.* **2018**, *121*, 253001.
- (18) Butts, D. A.; Rokhsar, D. S. Predicted signatures of rotating Bose–Einstein condensates. *Nature* **1999**, *397*, 327.
- (19) Madison, K. W.; Chevy, F.; Wohlleben, W.; Dalibard, J. Vortex formation in a stirred Bose–Einstein condensate. *Phys. Rev. Lett.* **2000**, *84*, 806–809.
- (20) Beinke, R.; Cederbaum, L. S.; Alon, O. E. Enhanced many-body effects in the excitation spectrum of a weakly interacting rotating Bose–Einstein condensate. *Phys. Rev. A: At., Mol., Opt. Phys.* **2018**, *98*, 053634.
- (21) Bloch, I.; Dalibard, J.; Zwerger, W. Many-body physics with ultracold gases. *Rev. Mod. Phys.* **2008**, *80*, 885–964.
- (22) Fetter, A. L. Rotating trapped Bose–Einstein condensates. *Rev. Mod. Phys.* **2009**, *81*, 647–691.
- (23) Post, E. J. Sagnac effect. *Rev. Mod. Phys.* **1967**, *39*, 475–493.
- (24) Shen, J.; He, S.; Zhuang, F. Aharonov–Carmi effect and energy shift of valence electrons in rotating C_{60} molecules. *Eur. Phys. J. D* **2005**, *33*, 35–38.
- (25) Merlin, R. Rotational anomalies of mesoscopic rings. *Phys. Lett. A* **1993**, *181*, 421–423.
- (26) Vignale, G.; Mashhoon, B. Persistent current in a rotating mesoscopic ring. *Phys. Lett. A* **1995**, *197*, 444–448.
- (27) Dvornikov, M. Galvano-rotational effect induced by electro-weak interactions in pulsars. *J. Cosmol. Astropart. Phys.* **2015**, *2015*, 037.
- (28) Matsuo, M.; Ieda, J.; Saitoh, E.; Maekawa, S. Effects of mechanical rotation on spin currents. *Phys. Rev. Lett.* **2011**, *106*, 076601.
- (29) Chowdhury, D.; Basu, B. Effect of spin rotation coupling on spin transport. *Ann. Phys. (Amsterdam, Neth.)* **2013**, *339*, 358–370.
- (30) Oliveira, A. B.; Bakke, K. Some aspects of an induced electric dipole moment in rotating and non-rotating frames. *R. Soc. Open Sci.* **2017**, *4*, 170541.
- (31) Cohen Tannoudji, C.; Dupont-Roc, J.; Grynberg, G. *Atom-Photon Interactions: Basic Processes and Applications*; Wiley: Weinheim, 2004.
- (32) Galego, J.; Garcia-Vidal, F. J.; Feist, J. Cavity-induced modifications of molecular structure in the strong-coupling regime. *Phys. Rev. X* **2015**, *5*, 041022.
- (33) Vendrell, O. Coherent dynamics in cavity femtochemistry: Application of the multi-configuration time-dependent Hartree method. *Chem. Phys.* **2018**, *509*, 55–65.
- (34) Wilkinson, J. H. *The Algebraic Eigenvalue Problem*; Clarendon Press: Oxford, 1965.
- (35) Walter, O.; Cederbaum, L. S.; Schirmer, J. The eigenvalue problem for “arrow” matrices. *J. Math. Phys. (Melville, NY, U. S.)* **1984**, *25*, 729–737.
- (36) O’Leary, D.; Stewart, G. Computing the eigenproblem and eigenvectors of arrowhead matrices. *J. Comput. Phys.* **1990**, *90*, 497–505.
- (37) Köppel, H.; Domcke, D.; Cederbaum, L. S. Multimode molecular dynamics beyond the Born–Oppenheimer approximation. *Adv. Chem. Phys.* **2007**, *57*, 59–246.
- (38) *Conical Intersections*; Domcke, W., Yarkony, D. R., Köppel, H., Eds.; World Scientific: Singapore, 2004.
- (39) Moiseyev, N.; Sindelka, M.; Cederbaum, L. S. Laser-induced conical intersections in molecular optical lattices. *J. Phys. B: At., Mol. Opt. Phys.* **2008**, *41*, 221001.

- (40) Halász, G. J.; Vibók, A.; Sindelka, M.; Moiseyev, N.; Cederbaum, L. S. Conical intersections induced by light: Berry phase and wavepacket dynamics. *J. Phys. B: At., Mol. Opt. Phys.* **2011**, *44*, 175102.
- (41) Halász, G. J.; Vibók, A.; Cederbaum, L. S. Direct signature of light-induced conical intersections in diatomics. *J. Phys. Chem. Lett.* **2015**, *6*, 348–354.
- (42) Csehi, A.; Kowalewski, M.; Halasz, G. J.; Vibok, A. Ultrafast dynamics in the vicinity of quantum light-induced conical intersections. *New J. Phys.* **2019**, *21*, 093040.
- (43) Badanko, P.; Hálász, G. J.; Csaszar, A. G.; Cederbaum, L. S.; Vibok, A.; Csehi, A. Substantial impact of the orientation of transition dipole moments on the dynamics of diatomics in laser fields. *J. Chem. Phys.* **2018**, *149*, 181101.
- (44) Polonyi, J. *Lecture Notes, Quantum Mechanics II*; University of Strasbourg: Strasbourg, 2020.
- (45) Demekhin, P. V.; Cederbaum, L. S. Light-induced conical intersections in polyatomic molecules: General theory, strategies of exploitation, and application. *J. Chem. Phys.* **2013**, *139*, 154314.