Berry phases and profiles of line wings and rainbow satellites induced by optical collisions

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The concept of Berry phase is included in an analysis of the intensity distribution in far wings of pressure-broadened spectral lines emitted or absorbed by atoms placed in an external cone-rotating electric field. Particular attention is focused on frequency regions where rainbow satellite bands appear. A classical-path treatment that employs the time-dependent Schrödinger equation is used to derive an expression for the line shape, and it uses a dipole transition moment calculated with quasimolecular wave functions given by the Berry version of the adiabatic approximation. It is found that in the presence of an external rotating electric field, the intensity distribution in far wings can be expressed in terms of the universal line shape function of the unified Franck-Condon theory once energy shifts due to Stark and Berry effects are taken into account. We show that the influence of Berry phase in the profiles of the far wings can be manifested either in the form of deviations of observed profiles from the quasistatic distribution or the appearance of additional features in the vicinity of the maximum of the rainbow satellite band. As an example, the modification of the rainbow satellite at 162.3 nm in the red wing of the self-broadened Lyman-α line of hydrogen, caused by an external rotating electric field, is considered.

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I. INTRODUCTION

Matveev and Musakhanov [1,2] have analyzed the appearance of the geometric Berry phase for an atom placed in an external electric field $\mathbf{F}(t)$ rotating with period τ around a cone about the laboratory axis z at fixed polar angle ϑ and constant angular velocity $\omega_F = d\varphi/dt = 2\pi/\tau$. It is known [3,4] that in the limit of slow rotation on a closed path such that after the time $t = \tau$ the electric field $\mathbf{F}(\tau)$ returns to its original value $\mathbf{F}(0)$, the atomic wave function $|\phi_m\rangle$ acquires a geometric phase [3–5]

$$\gamma_m(\tau) = -m\Theta_F(\tau), \tag{1}$$

where

$$\Theta_F(\tau) = 2\pi(1 - \cos\vartheta) \tag{2}$$

is the solid angle subtended by the cone, and m is the quantum number of the angular momentum projection onto the quantization axis. From a spectroscopic point of view

$$\frac{\gamma_m(\tau)}{\tau} = -\frac{m\Theta_F(\tau)}{\tau} = -m(1 - \cos\vartheta)\omega_F = \delta_m \tag{3}$$

is a measure of the shift δ_m of the energy of the level $|\phi_m\rangle$ in angular frequency units caused by the time rate of change of Berry phase [6]. Thus in case of transitions between two levels whose m values differ by Δm, there will be a contribution to the transition frequency of $\Delta m\Theta_F(\tau)/\tau$. This means that in the cone-rotating field one can expect the appearance of a "Berry splitting" of spectral lines that superimposes on that due to the linear (for hydrogenlike atoms) or quadratic Stark effect caused by the electric field which in the rotating reference frame (x', y', z') is assumed here to be constant ($F = |F| = \text{const}$) and directed along the z' axis.

Starting from the zero-approximation wave functions of the hydrogen atom in parabolic coordinates and using the rotation matrix $\hat{D}(\omega_F t, \vartheta, 0)$ for the Euler angles $(\omega_F t, \vartheta, 0)$ the authors of Refs. [1,2] derived a formula for intensities and spectral positions of various Berry components. To our knowledge, however, the Berry splitting of the type predicted by them has not yet been observed, and their formula has not been verified experimentally. Nevertheless, in a recent paper by Difallah *et al.* [7] the Berry splitting of optical lines has been taken into account in their calculations of profiles of the Stark-broadened Lyman-α line emitted from a plasma subjected to a rotating electric field. Results of their calculations, which were performed in the framework of an adiabatic approximation, seem to indicate the importance of the effect caused by Berry phase, at least for the core region of the Lyman-α line.

In the present work, unlike Ref. [7], we are concerned with the shapes of far wings of pressure-broadened lines of atoms placed with perturbing particles in a cone-rotating external electric field [8,9]. The main goal of this paper is to assess consequences of the inclusion of the energy-level shifts due to Berry phase into an analysis of the intensity distribution in the far wings, particularly in those frequency regions where rainbow satellite bands appear. Our discussion is based on a simplified model and as such it has rather a qualitative character. First of all, we try to answer the question whether or not Berry phases play any role in the formation of pressure-broadened spectral line shapes. A positive answer to this question seems to follow from an analysis due to Zygelman [10], who demonstrated the appearance of the geometric phase in the context of collision problems involving bound and free diatomic systems. Moreover, he suggested that the effects of geometric phase should be seen on the profiles of collision-broadened spectral lines found in a gas at low temperatures. This was based on an analysis of corrections to the interatomic potentials caused by the coupling of the relative nuclear motion with a non-Abelian gauge field. However, pressure broadening theory was not invoked in Zygelman's

analysis, and the effect of an external rotating electric field was not considered.

II. BERRY SPLITTINGS

In our model the radiating atom is taken to be fixed at the center of a macroscopic container placed in an external cone-rotating electric field $\mathbf{F}(t)$ of constant magnitude $F = |\mathbf{F}| =$ const, and we investigate the broadening due to the interaction with all N perturbing atoms present in the container. Let $\mathbf{R} \equiv \{\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N\}$ be the set of coordinates of the perturbers, and $\mathbf{r}$ a set of coordinates of the electrons of the radiating atom. We consider the case of an isolated spectral line corresponding to the transition between a single initial state n_i and a single final state n_f in the unperturbed radiator, i.e., when all $\mathbf{R}_i \longrightarrow \infty$ $(i = 1,2,\ldots,N)$ and the field vanishes $(\mathbf{F} = \mathbf{0})$. The spectral position of this line is determined by the "unperturbed" frequency $\omega_0 = (E_i^0 - E_f^0)/\hbar$, where E_i^0 and E_f^0 denote energies of the unperturbed initial and final atomic states $|\varphi_{n_i}^0\rangle$ and $|\varphi_{n_f}^0\rangle$, respectively. Following Jabłoński [11] and Baranger [12], we treat the assembly of one radiating atom and N perturbers here as a huge $(N+1)$-atom quasimolecule driven by a time-dependent Hamiltonian $\hat{H}(t) = \hat{H}(\mathbf{r},\mathbf{F}(t),\mathbf{R}(t))$. A characteristic quasimolecular feature is the replacement of the fixed energy level of each atomic state $|\varphi_{n_i}^0\rangle$ and $|\varphi_{n_f}^0\rangle$ with an energy surface whose value varies with the instantaneous perturber configuration. The transitions between these surfaces are the source of pressure broadening phenomena.

We assume that the electric field $\mathbf{F}(t)$ varies adiabatically with time and returns to its initial value at time $t = \tau$. This means that the quasimolecule undergoes adiabatic cyclic evolution around a closed path $\mathbf{F}(t)$ in parameter space. The parameters $\mathbf{R}(t)$, on the other hand, generally display the translational motion of perturbers and vary over the range $0 < |\mathbf{R}| < \infty$.

Suppose that the initial state $|\Psi_{n_i}(t)\rangle$ of the quasimolecule evolves according to the Schrödinger equation

$$\hat{H}(t)\big|\Psi_{n_i}(t)\big\rangle = i\hbar\frac{d}{dt}\big|\Psi_{n_i}(t)\big\rangle, \tag{4}$$

and similarly for the final state $|\Psi_{n_f}(t)\rangle$. Let $|\phi_{n_i}(\mathbf{r},\mathbf{F},\mathbf{R})\rangle$ and $|\phi_{n_f}(\mathbf{r},\mathbf{F},\mathbf{R})\rangle$ be the eigenfunction solutions of

$$\hat{H}(\mathbf{r},\mathbf{F},\mathbf{R})\big|\phi_{n_i}(\mathbf{r},\mathbf{F},\mathbf{R})\big\rangle = W_{n_i}(\mathbf{F},\mathbf{R})\big|\phi_{n_i}(\mathbf{r},\mathbf{F},\mathbf{R})\big\rangle \tag{5}$$

with eigenenergy $W_{n_i}(\mathbf{F},\mathbf{R})$ for the initial state and $W_{n_f}(\mathbf{F},\mathbf{R})$ for the final state.

As shown by Berry [13], in the adiabatic approximation the solutions of Eq. (4) can be written

$$\big|\Psi_{n_i}(t)\big\rangle = \exp\left\{-\frac{i}{\hbar}\int_0^t dt' W_{n_i}(\mathbf{F}(t'),\mathbf{R}(t'))\right\} \times \exp\big\{i\gamma_{n_i}(t)\big\}\big|\phi_{n_i}(\mathbf{r},\mathbf{F}(t),\mathbf{R}(t))\big\rangle \tag{6}$$

and similarly for $|\Psi_{n_f}(t)\rangle$. The first exponential in Eq. (6) is the familiar dynamic phase factor. The extra phases γ_{n_i} and γ_{n_f} are Berry phases that become physically important for cyclic evolution. In our case such an evolution is related to the circuit described by the external electric field $\mathbf{F}$ as it rotates from $t = 0$ to $t = \tau$. Inserting Eq. (6) into Eq. (4) and using Eq. (5) yields the fundamental formula for the Berry phase [13–15]

$$\gamma_{n_i}(t) = i\int_0^t dt'\big\langle\phi_{n_i}(\mathbf{F}(t'))\big|\frac{d}{dt'}\big|\phi_{n_i}(\mathbf{F}(t'))\big\rangle, \tag{7}$$

and similarly for $\gamma_{n_f}(t)$. Here we have suppressed the explicit dependence on the electron positions $\mathbf{r}$ and the perturber coordinates $\mathbf{R}(t)$. Note that generally the perturbers surrounding the radiating atom do not move along closed paths, and therefore the time dependence of $\mathbf{R}(t)$ does not contribute consistently to energy shifts like those induced by cyclic motion as in the Berry phase.

To justify the neglect of contributions to the Berry phase coming from open-ended paths of perturbers, one usually invokes the Born-Fock gauge transformation for a given path in the $\mathbf{R}$ space such that the corresponding vector gauge potential

$$\mathbf{A}(\mathbf{R}) = i\langle\phi_n(\mathbf{r},\mathbf{F},\mathbf{R})|\nabla_R|\phi_n(\mathbf{r},\mathbf{F},\mathbf{R})\rangle,$$

vanishes. Several researches have noted [16–18], however, that this choice of gauge is not always possible globally, so that Berry phase may also appear in a noncyclic evolution. However, the Born-Fock gauge can cause the transformed vector potential to vanish if the curl of $\mathbf{A}(\mathbf{R})$ is zero. In the present work we are concerned specifically with the wings and satellite features at the Lyman-α line of hydrogen associated with the free-free transitions between the $X\,^1\Sigma_g^+$ and $B\,^1\Sigma_g^+$ molecular states. For these two states the quantum number Λ of the projection of the electronic orbital angular momentum along the interatomic axis is equal to zero. Zygelman [10] has shown that for the Σ states $(\Lambda = 0)$ of diatomic molecules the only nonvanishing term of the vector gauge potential is its radial component, and thus the curl of $\mathbf{A}(\mathbf{R})$ vanishes at all $\mathbf{R}$. This means that in this case, the vector potential can be eliminated by the Born-Fock gauge transformation, and the contributions to the Berry phase effects coming from paths in $\mathbf{R}$ space do not occur on spectral line profiles associated with the $\Sigma - \Sigma$ transitions. Nevertheless, in principle they can occur for spectral transitions involving molecular states with $\Lambda \neq 0$, and these cases require further more detailed study.

More generally, however, the neglect of the time dependence of the perturber coordinates $\mathbf{R}(t)$ is justified in the quasistatic approximation used here to describe the far wings of a line profile, because the autocorrelation time there is so short that the change in $\mathbf{R}_i(t)$ for $i = 1,2,\ldots,N$ during that time is negligible.

If we express the electric field $\mathbf{F}(t) = \mathbf{F}(\vartheta,\varphi)$ as a function of spherical angles $\vartheta = \vartheta(t)$ and $\varphi = \varphi(t) = \omega_F t$, then the wave functions at time t are connected with those in the rotating reference frame aligned with $\mathbf{F}$, where $\vartheta = 0$ and $\varphi = 0$, by the rotational transformation

$$\big|\phi_{n_i}(\mathbf{F}(t))\big\rangle \equiv \big|\phi_{n_i}(\vartheta,\varphi,F)\big\rangle = \hat{U}(t)\big|\phi_{n_i}(0,0,F)\big\rangle, \tag{8}$$

where

$$\hat{U}(t) = \exp\left(-\frac{i}{\hbar}\hat{l}_z\varphi\right)\exp\left(-\frac{i}{\hbar}\hat{l}_y\vartheta\right) \tag{9}$$

with $\hat{l}_y$ and $\hat{l}_z$ being the operators for the projection of the angular momentum onto the y and z axes, respectively.

Without the external field, the unperturbed wave functions $|\phi_n^0\rangle$ of a hydrogenlike atom with the nucleus of charge Ze are

eigenstates $|n,l,m\rangle$ of energy E_n^0, orbital angular momentum l, and its projection m on the z axis. Here we confine ourselves to the cases of low Z hydrogenic atoms, for which we can neglect the fine-structure term in the Hamiltonian. The spin of the electron is therefore not important to our discussion. Of course, for higher Z, this simplification fails and the fine-structure splitting of the $n = 2$ level must be taken into account [19]. In the presence of the rotating electric field $\mathbf{F}(t)$ directed along the z' axis, the perturbation operator eFz' gives rise to the Stark splitting among the levels of energy E_n^0. In the rotating reference frame the electric field is constant. First-order perturbation theory gives the energies $E_n^{n_2-n_1,m}(F)$ of the Stark sublevels: [20]

$$E_n^{n_2-n_1,m}(F) = E_n^0 + \Delta E_n^{n_2-n_1,m}(F), \tag{10}$$

where the shift in energy is

$$\Delta E_n^{n_2-n_1,m}(F) = \frac{3a_0e}{2Z} Fn(n_2 - n_1).$$

Here n_1 and n_2 are parabolic quantum numbers related to the principal quantum number n by $n = n_1 + n_2 + m + 1$.

The change in the perturbation Hamiltonian eFz' due to the cone precession of the external electric field can be found by applying (ϑ,φ)-dependent rotations [14]. One obtains then for the Berry phase $\gamma_m(t)$ at time t

$$\gamma_m(t) = \frac{1}{\tau}\gamma_m(\tau)t, \tag{11}$$

where $\gamma_m(\tau)$ is given by Eq. (1) and represents the total Berry phase corresponding to a closed path with $\mathbf{F}(\tau) = \mathbf{F}(0)$. Thus the Berry phase at time t can be written

$$\gamma_m(t) = -m\Theta_F(t), \tag{12}$$

where

$$\Theta_F(t) = (1 - \cos\vartheta)\omega_F t. \tag{13}$$

The time derivative $\dot{\gamma}_m(t)$ satisfies

$$\dot{\gamma}_m(t) = \frac{1}{\tau}\gamma_m(\tau) = \delta_m \tag{14}$$

in accordance with Eq. (3), and $\hbar\delta_m$ is the energy shift of the level $|\phi_m\rangle$ due to the Berry phase effect.

The adiabatic energies $W_{n_i}(\mathbf{F},\mathbf{R})$ and $W_{n_f}(\mathbf{F},\mathbf{R})$ defined by Eq. (5) can then be expressed as

$$W_{n_i}(\mathbf{F},\mathbf{R}) = E_{n_i}^0 + \Delta E_{n_i}^{\alpha_i}(F) + V_{n_i}^{\alpha_i}(\mathbf{R}), \tag{15}$$

and

$$W_{n_f}(\mathbf{F},\mathbf{R}) = E_{n_f}^0 + \Delta E_{n_f}^{\alpha_f}(F) + V_{n_f}^{\alpha_f}(\mathbf{R}), \tag{16}$$

where α_i and α_f label the quantum numbers (l,m) or (n_1,n_2,m) that characterize the Stark and Berry sublevels of the initial and final states. Here $V_{n_i}^{\alpha_i}(\mathbf{R})$ and $V_{n_f}^{\alpha_f}(\mathbf{R})$ are the adiabatic potentials describing the interaction between perturbers and the radiating atom in its initial and final state, respectively.

An important issue in the approach under consideration is that the rotation of the external electric field must be slow in the time scale of the quantum system, i.e. adiabatic with respect to transitions between sublevels for different m. To find the criterion for adiabaticity we follow Berry's work [13] and note that in the adiabatic limit the system remains in an eigenstate of the instantaneous Hamiltonian. This means that the quantum number m of the projection of the angular momentum onto the axis z' does not change during the rotation of this axis. Thus for the adiabatic approach to be valid, the period $\tau = 2\pi/\omega_F$ of the rotation must be greater than the characteristic time $\hbar/\Delta E_{n_i}^{\alpha_i}$. For the Lyman-series lines, the criterion to be fulfilled by the strength F and angular frequency ω_F of an external adiabatically cone-rotating electric field is

$$\omega_F < \frac{3\pi a_0 en(n_2 - n_1)}{Z\hbar} F. \tag{17}$$

This criterion resembles that put forward a long time ago by Klein and Margenau [21] on the basis of Spitzer's work [22] for the case of adiabatic collisions. It is also close to a "quasistatic" criterion given by Peyrusse [19]. An alternative criterion was proposed by Matveev and Musakhanov [1,2], who consider the wave function $|\Psi'(t)\rangle$ in a rotating reference frame that is related to the wave function $|\Psi(t)\rangle$ in a fixed reference frame by $|\Psi'(t)\rangle = U^+(t)|\Psi(t)\rangle$ in accordance with Eq. (9). Their condition for the adiabatic approximation is reduced to the requirement that the "magnetic" interaction $i\hbar\dot{U}^+(t)U(t)$ induced by the rotation be small, i.e.,

$$\left|\left\langle\phi_{n_i,\alpha_i}\right|\hbar\dot{U}^+(t)U(t)\left|\phi_{n_i,\alpha_i}\right\rangle\right| \ll \left|\Delta E_{n_i}^{\alpha_i}\right|. \tag{18}$$

Estimations presented in Refs. [1] and [2] indicate that this criterion is equivalent to that given by Eq. (17).

III. INCLUSION OF BERRY PHASE INTO LINE SHAPE FORMULA

Following Anderson [23] and Sobelman [24] the intensity distribution $I_{n_i,n_f}(\omega)$ of the collisionally broadened spectral line corresponding to the $|\phi_{n_i}\rangle \to |\phi_{n_f}\rangle$ electric-dipole transition is given by

$$I_{n_i,n_f}(\omega) = \frac{1}{2\pi}\left\langle\left|\int_{+\infty}^{\infty} dt\, er_{n_i,n_f}(t)e^{-i\omega t}\right|^2\right\rangle_{\mathrm{Av}}, \tag{19}$$

where the symbol $\langle\cdots\rangle_{\mathrm{Av}}$ denotes the average over collisions, and

$$er_{n_i,n_f}(t) = e\left\langle\Psi_{n_i}(t)\right|\hat{r}\left|\Psi_{n_f}(t)\right\rangle \tag{20}$$

is the electric-dipole transition moment of the $(N+1)$-atomic quasimolecule consisting of an optically active atom and N neutral perturbers. At perturber densities sufficiently low that essentially only binary collisions occur, the wings of spectral lines are described by the intensity distribution radiated when only one perturber is present [25–27]. This corresponds to the one-perturber approximation in which the wave functions $|\Psi_{n_i}(t)\rangle$ and $|\Psi_{n_f}(t)\rangle$ are assumed to be given by the adiabatic formulas, Eq. (6), where now $\mathbf{R}$ denotes the coordinates of the single perturber $(N = 1)$.

In the presence of an external cone-rotating electric field, the initial $|\phi_{n_i}\rangle$ and final $|\phi_{n_f}\rangle$ electronic states split into several Stark and Berry components labeled by the indices α_i and α_f. We denote these wave functions below simply by $|\phi_{\alpha_i}\rangle$ and $|\phi_{\alpha_f}\rangle$. They are calculated in the rotating reference frame (x',y',z'), whereas the intensity distribution in Eq. (19) is the spectrum measured in the laboratory with its fixed coordinates. Using the Wigner rotation functions $D^j_{m,m'}(\varphi,\vartheta,0)$ one can express the line shape in terms of the spherical

components $er_{m'}$ of the dipole transition moment. Since we consider here the cases of spectral lines of the Lyman -series of low-Z hydrogenlike atoms, the upper states correspond to the value $l = 1$ of the quantum number for the orbital angular momentum, while the lower state is the ground state ($n = 1$) with $l = 0$. Following Matveev and Musakhanov [1,2] and making use of Eqs. (6), (15), (16), and (20), the intensity distribution in Eq. (19) can then be written

$$I_{n_i,n_f}(\omega) = \frac{1}{G}\sum_{\alpha_i,m,m'} \left|d^1_{m,m'}\right|^2 \left|\langle\phi_{\alpha_i}\left|er_{m'}\right|\phi_{\alpha_f}\rangle\right|^2 J\left(\xi_{\alpha_i,\alpha_f}\right), \tag{21}$$

where

$$G = \sum_{\alpha_i,m,m'} \left|d^1_{m,m'}\right|^2 \left|\langle\phi_{\alpha_i}\left|er_{m'}\right|\phi_{\alpha_f}\rangle\right|^2 \tag{22}$$

is the normalization factor, and $d^1_{m,m'} = D^1_{m,m'}(0,\vartheta,0)$ are the Wigner rotation functions for the matrix elements of the spherical components of the dipole transition moment $er_{m'}$ with $er_0 = ez'$, and $er_{\pm1} = \mp e(x' \pm y')/\sqrt{2}$. In Eq. (21) the function $J(\xi_{\alpha_i,\alpha_f})$ describes the shape of the $\alpha_i \to \alpha_f$ components of the $n_i \to n_f$ spectral line and is defined by

$$J\left(\xi_{\alpha_i,\alpha_f}\right) = \frac{1}{2\pi}\left\langle\left|A\left(\xi_{\alpha_i,\alpha_f}\right)\right|^2\right\rangle_{\mathrm{Av}}, \tag{23}$$

where

$$A\left(\xi_{\alpha_i,\alpha_f}\right) = \int_{-\infty}^{+\infty} dt\ \exp\left\{-i\,\Phi_{\alpha_i,\alpha_f}(t)\right\}, \tag{24}$$

and

$$\Phi_{\alpha_i,\alpha_f}(t) = \xi_{\alpha_i,\alpha_f}t - \frac{1}{\hbar}\int_0^t dt'\Delta V_{\alpha_i,\alpha_f}(t'). \tag{25}$$

Here

$$\xi_{\alpha_i,\alpha_f} = \omega - \Omega_{\alpha_i,\alpha_f} \tag{26}$$

denotes the frequency displacement relative to the frequency $\Omega_{\alpha_i,\alpha_f}$ defined as

$$\Omega_{\alpha_i,\alpha_f} = \omega_0 + \Delta\omega^F_{\alpha_i,\alpha_f} + \left(\delta_{\alpha_f} - \delta_{\alpha_i}\right), \tag{27}$$

where

$$\Delta\omega^F_{\alpha_i,\alpha_f} = \frac{1}{\hbar}\left[\Delta E_{\alpha_f}(F) - \Delta E_{\alpha_i}(F)\right]. \tag{28}$$

The discrete frequency $\Omega_{\alpha_i,\alpha_f}$ gives the spectral position of the component $\alpha_i \to \alpha_f$ formed by the Stark and Berry splitting of the $n_i \to n_f$ transition in the external cone-rotating electric field. In the absence of the field we have $\Omega_{\alpha_i,\alpha_f} = \omega_0$.

In the following we adopt the classical-path approximation with trajectories determined by the interaction potential surface of the initial state. The symbol $\langle\cdots\rangle_{\mathrm{Av}}$ in Eq. (23) denotes then the average over impact parameters ρ and initial energies $E_i = \mu v^2/2$ of their relative motion, where μ is the reduced mass. Equation (23) can then be reexpressed in the form

$$J\left(\xi_{\alpha_i,\alpha_f}\right) = \int_0^\infty dE_i\, f(E_i)\int_0^\infty d\rho\ \rho\left|A\left(\xi_{\alpha_i,\alpha_f}\right)\right|^2, \tag{29}$$

where $f(E_i)$ is the Maxwellian distribution of initial energies.

IV. FAR WINGS

Now we focus our attention on the behavior of $A(\xi_{\alpha_i,\alpha_f})$, Eq. (24), at large values of ξ_{α_i,α_f}, i.e., for frequencies in the far wings of the $n_i \to n_f$ transition. At large ξ_{α_i,α_f}, the rapidly oscillating integrand in Eq. (24) contributes significantly to $A(\xi_{\alpha_i,\alpha_f})$ mainly in regions of stationary phase, i.e., near points t_C at which the first time derivative is zero:

$$\dot{\Phi}_{\alpha_i,\alpha_f}(t_C) = 0. \tag{30}$$

According to Eq. (25) these stationary-phase points are solutions of the equation

$$\hbar\xi_{\alpha_i,\alpha_f} = \Delta V_{\alpha_i,\alpha_f}(R_C), \tag{31}$$

where $R_C = R(t_C)$ denotes the interatomic separation at time t_C. In the absence of a rotating external electric field, i.e., when both the Stark ($\Delta\omega^F_{\alpha_i,\alpha_f}$) and Berry ($\delta_{\alpha_i}$ and δ_{α_f}) displacements vanish, Eq. (31) becomes

$$\hbar(\omega - \omega_0) = \Delta V_{\alpha_i,\alpha_f}\left(R^0_C\right). \tag{32}$$

In line-broadening theories based on the Franck-Condon principle, this equation defines the Condon points R^0_C identified as positions at which, according to the classical formulation of the principle, transitions occur [8,9,11,28]. Such an identification is certainly appropriate when R^0_C or R_C are real. However, solutions of Eq. (30) or (31) may be complex. As the saddle points of $\Phi_{\alpha_i,\alpha_f}(t)$ they can also contribute to the intensity distribution at line wings [8,9,28]. By comparing Eqs. (31) and (32) we conclude that R_C are the ordinary Condon points once the energy shifts caused by Berry phase and Stark effects are taken into account.

A. Effect of Berry phase on the quasistatic profile

If the phase function $\Phi_{\alpha_i,\alpha_f}(t)$ is approximated by a quadratic expansion around t_C, then after substitution into Eq. (24) one obtains from Eq. (29) the quasistatic formula for the profile $J_{\mathrm{QS}}(\xi_{\alpha_i,\alpha_f})$ of the $\alpha_i \to \alpha_f$ component of the $n_i \to n_f$ spectral line: [26,27]

$$J_{\mathrm{QS}}\left(\xi_{\alpha_i,\alpha_f}\right) = \frac{4\pi R_C^2}{\left|\Delta V'_{\alpha_i,\alpha_f}(R_C)\right|}\exp\left(-\frac{V_{\alpha_i}(R_C)}{k_B T}\right), \tag{33}$$

where $\Delta V'_{\alpha_i,\alpha_f}(R_C) \equiv \left(d\Delta V_{\alpha_i,\alpha_f}/dR\right)_{R_C}$, k_B is the Boltzmann constant, and T is the temperature.

Suppose, for example, that the interatomic interactions in the region of interest take the van der Waals form $\Delta V_{\alpha_i,\alpha_f}(R) = \hbar\Delta C_6^{i,f} R^{-6}$, where $\Delta C_6^{i,f}$ denotes the difference of van der Waals constants for the initial and final states. Equation (33) yields [for $V_{\alpha_i}(R_C) \ll k_B T$]

$$J_{\mathrm{QS}}\left(\xi_{\alpha_i,\alpha_f}\right) \equiv J^{\mathrm{BC}}_{\mathrm{QS}}\left(\xi_{\alpha_i,\alpha_f}\right) = \frac{2\pi}{3}\left|\Delta C_6^{i,f}\right|^{1/2}\left|\xi_{\alpha_i,\alpha_f}\right|^{-3/2}. \tag{34}$$

Here the superscript "BC" relates to Condon points R_C determined on the basis of Eq. (31), i.e., when the Berry phase effect is taken into account. In the absence of the external rotating field we have $\xi_{\alpha_i,\alpha_f} = \omega - \omega_0$, and then Eq. (34)

becomes

$$J_{\rm QS}(\xi_{\alpha_i,\alpha_f}) \equiv J^C_{\rm QS}(\omega-\omega_0) = \frac{2\pi}{3}\left|\Delta C_6^{i,f}\right|^{1/2}|\omega-\omega_0|^{-3/2}, \tag{35}$$

where the superscript "C" refers to the Condon points R_C^0 as defined by Eq. (32). This is Kuhn's familiar "3/2 relation" for the shape of the wing of a spectral line broadened due to van der Waals forces, and it was supported by his observation of the wing of the mercury resonance line (253.7 nm) perturbed by argon [29], and by Minkowski [30] with the wings of sodium D lines perturbed by argon, as well as by other researchers [27,31].

A comparison of Eqs. (34) and (35) leads to the conclusion that in systems for which the van der Waals potential may be applied, the far wings of pressure-broadened spectral lines emitted or absorbed by a gas placed in an external rotating electric field should include the appearance of the Berry phase effect in collisionally perturbed optical spectra. The ratio of the "Berry-Condon-Kuhn" quasistatic distribution, Eq. (34), to the ordinary "Condon-Kuhn" quasistatic distribution, Eq. (35), is

$$\frac{J^{\rm BC}_{\rm QS}(\xi_{\alpha_i,\alpha_f})}{J^C_{\rm QS}(\omega-\omega_0)} = \frac{|\omega-\omega_0|^{3/2}}{\left|\omega-\omega_0-\Delta\omega^F_{\alpha_i,\alpha_f}-\left(\delta_{\alpha_i}-\delta_{\alpha_f}\right)\right|^{3/2}}. \tag{36}$$

In accordance with Eq. (27) the values of this ratio depend on the strength F and the angular frequency ω_F of the rotating electric field as well as on the angle ϑ.

B. Effects of Berry phase on rainbow satellite bands

The general form of the quasistatic distribution, Eq. (33), gives infinite intensity at frequency displacements $\xi^S_{\alpha_i,\alpha_f}$ satisfying

$$\hbar\xi^S_{\alpha_i,\alpha_f} = \Delta V_{\alpha_i,\alpha_f}(R_S), \tag{37}$$

where R_S is the distance between the radiating atom and the perturber at which the difference potential has an extremum. As the Condon point R_C approaches a position R_S, the derivative in the denominator of Eq. (33) vanishes and the quasistatic distribution becomes singular. These quasistatic singularities, which occur wherever the forces acting on the radiating atom in its initial and final state are equal, are usually designated "classical rainbow satellites" because of their analogy to the classical theory of the formation of rainbows by light scattering [25].

As follows from Eqs. (25), (30), and (37), in the presence of an external rotating electric field the spectral ("Berry-Condon") position $\omega_S^{\rm BC}$ of the classical rainbow singularity is given by

$$\omega_S^{\rm BC} = \omega_0 + \frac{1}{\hbar}\Delta V_{\alpha_i,\alpha_f}(R_S) + \Delta\omega^F_{\alpha_i,\alpha_f} + \delta_{\alpha_f} - \delta_{\alpha_i}. \tag{38}$$

Without the external field, when both the Stark and the Berry shifts disappear, the rainbow singularity occurs at the "Condon" frequency ω_S^C given by

$$\omega_S^C = \omega_0 + \frac{1}{\hbar}\Delta V_{\alpha_i,\alpha_f}(R_S). \tag{39}$$

A comparison of Eqs. (38) and (39) shows that in the presence of the cone-rotating electric field, the Berry phases result in a shift in the position of the classical rainbow satellite with respect to that produced in the absence of that field.

Suppose $\Delta V_{\alpha_i,\alpha_f}(R)$ has a minimum value $-\hbar\varepsilon$ at $R = R_S$ (with $\varepsilon > 0$). Then in the vicinity of R_S, the function $\Delta V_{\alpha_i,\alpha_f}(R)$ may be approximated by a quadratic expansion:

$$\Delta V_{\alpha_i,\alpha_f}(R) \approx -\hbar\varepsilon + \frac{1}{2}\Delta V''_{\alpha_i,\alpha_f}(R_S)[R-R_S]^2, \tag{40}$$

where $\Delta V''_{\alpha_i,\alpha_f}(R_S)$ is positive since $\Delta V_{\alpha_i,\alpha_f}(R_S) = -\hbar\varepsilon$ is a minimum. According to Eq. (31) the Condon points

$$R_C = R_S \pm \left[\frac{2\hbar\left(\xi_{\alpha_i,\alpha_f}+\varepsilon\right)}{\Delta V''_{\alpha_i,\alpha_f}(R_S)}\right]^{1/2} \tag{41}$$

are real if $\xi_{\alpha_i,\alpha_f} > -\varepsilon \equiv \xi^S_{\alpha_i,\alpha_f}$. In this case the rainbow singularity appears in the red wing of the spectral line. Beyond the classical rainbow frequency, i.e., for $\xi_{\alpha_i,\alpha_f} < -\varepsilon$, solutions of Eq. (31) are a complex conjugate pair of Condon points

$$R_C = R_S \pm i\left[\frac{2\hbar\left(\left|\xi_{\alpha_i,\alpha_f}\right|-\varepsilon\right)}{\Delta V''_{\alpha_i,\alpha_f}(R_S)}\right]^{1/2}. \tag{42}$$

As shown first by Sando and Wormhoudt [28] the contribution to the intensity distribution from complex points of stationary phase falls off exponentially with increasing separation of R_C from the real R axis.

1. Airy function approximation

Due to its divergence at $\omega_S^{\rm BC}$ or ω_S^C, i.e., when R_C or R_C^0 approaches R_S, the quasistatic distribution, Eq. (33), becomes unrealistic and predicts an infinite spike in the spectrum there instead of a continuous satellite maximum located in the line wings. To avoid the divergence problem we adopt an extended stationary phase method in which the phase function $\Phi_{\alpha_i,\alpha_f}(t)$ in Eq. (24) is approximated by a cubic expansion around t_C. Then $A(\xi_{\alpha_i,\alpha_f})$ in Eq. (24) can be expressed in terms of the regular homogenous Airy function. Using arguments identical to those applied in the unified Franck-Condon (UFC) line shape treatment [8,9], and employing a method due to Sando and Wormhoudt [28] to perform the Maxwellian averaging in Eq. (29), we find

$$J\left(\xi_{\alpha_i,\alpha_f}\right) = \frac{48\hbar\pi R_C^2}{\left|\Delta V'_{\alpha_i,\alpha_f}(R_C)\right|}\left|z_{\alpha_i,\alpha_f}\right|^{1/2} \times L\left(z_{\alpha_i,\alpha_f}\right)\exp\left[-\frac{V_{\alpha_i}(R_C)}{k_BT}\right]. \tag{43}$$

Here

$$z_{\alpha_i,\alpha_f} = \frac{1}{2}\left(\frac{\mu}{k_BT}\right)^{1/3}\left(\frac{\Delta V'_{\alpha_i,\alpha_f}(R_C)}{\hbar}\right)^2\left|\frac{\Delta V''_{\alpha_i,\alpha_f}(R_C)}{\hbar}\right|^{-4/3} \tag{44}$$

is a dimensionless parameter that plays the role of a reduced frequency displacement, and

$$L\left(z_{\alpha_i,\alpha_f}\right) = \int_0^\infty dx\, x^{-2}Ai^2\left(-z_{\alpha_i,\alpha_f}x\right)\exp(-x^{-3}) \tag{45}$$

is the universal line-shape function of the UFC theory [8]. It should be emphasized, however, that all quantities here relate to the Condon point R_C and not to R_C^0 as in the original version of the UFC treatment. In accordance with Eq. (21) the resulting intensity distribution in the far wing of the $n_i \to n_f$ line emitted or absorbed by hydrogenlike atoms placed in a rotating electric field can be written

$$J(\xi_{\alpha_i,\alpha_f}) = \frac{24\hbar\pi}{G} \sum_{\alpha_i,m,m'} |d^1_{m,m'}(\vartheta)|^2 |\langle\phi_{\alpha_i}|er_{m'}|\phi_{\alpha_f}\rangle|^2 \times \frac{R_C^2 |z_{\alpha_i,\alpha_f}\pi|^{1/2}}{|\Delta V'_{\alpha_i,\alpha_f}(R_C)|} L(z_{\alpha_i,\alpha_f}) \exp\left[-\frac{V_{\alpha_i}(R_C)}{k_B T}\right], \tag{46}$$

where the normalization factor G is given by Eq. (22).

For real values of R_C, Eq. (41), the parameters z_{α_i,α_f} are always positive. For them, the general formula, Eq. (43), can be substantially simplified when the stationary phase points are located in the vicinity of the classical turning point, where $E_i = V_{\alpha_i}(R_C)$. As shown in Ref. [8], the dominant contribution to the integral in Eq. (45) then comes from large values of $z_{\alpha_i,\alpha_f} x$ and this yields asymptotically the quasistatic formula, Eq. (33). Obviously it is singular for $z_{\alpha_i,\alpha_f} = 0$, i.e., for Condon points located at extrema of the difference potential ($R_C \to R_S$). In the vicinity of R_S we can use the quadratic expansion, Eq. (40), where $\Delta V''_{\alpha_i,\alpha_f}(R_S)$ is assumed to be positive. This is justified for red rainbow satellites which are due to a minimum in $\Delta V_{\alpha_i,\alpha_f}(R_S)$. Using Eqs. (40), (41), and (43), one can show that for frequencies in the quasistatic part of the red wing of the $\alpha_i \to \alpha_f$ component of the $n_i \to n_f$ spectral line, the parameter z_{α_i,α_f} is positive and can be written

$$z_{\alpha_i,\alpha_f} = \left[\frac{\hbar\mu}{k_B T \Delta V''_{\alpha_i,\alpha_f}(R_S)}\right]^{1/3} (\xi_{\alpha_i,\alpha_f} + \varepsilon). \tag{47}$$

On the other hand, outside the classical rainbow frequency (for $\xi_{\alpha_i,\alpha_f} < -\varepsilon$) the intensity distribution is still determined by the universal function $L(z_{\alpha_i,\alpha_f})$, but now with a negative parameter z_{α_i,α_f}:

$$z_{\alpha_i,\alpha_f} = -\left[\frac{\hbar\mu}{k_B T \Delta V''_{\alpha_i,\alpha_f}(R_S)}\right]^{1/3} (|\xi_{\alpha_i,\alpha_f}| - \varepsilon). \tag{48}$$

As shown in Ref. [8] for large values of $-z_{\alpha_i,\alpha_f}$, Eq. (43) yields in the asymptotic limit the exponentially decreasing "antistatic" profile which is smaller than the quasistatic one by the factor $\exp[-12^{1/3}|z_{\alpha_i,\alpha_f}|]/\sqrt{3}$. As in the quasistatic case, the antistatic one is also singular for $z_{\alpha_i,\alpha_f} = 0$. The UFC profile of the rainbow satellite band given by Eq. (43) has no singularities at all, but its maximum does not occur at the classical rainbow satellite position $z_{\alpha_i,\alpha_f} = 0$, but rather at $z^{\max}_{\alpha_i,\alpha_f} = 0.328\,814$. This means that the maximum of the rainbow satellite band is located in the classically accessible region of interatomic separations, i.e., at real Condon points R_C for which the parameters z_{α_i,α_f} are positive. Its spectral position $\xi_{\max}$ can be determined from the condition

$$\xi_{\max} + \varepsilon = 0.328\,814 \left(\frac{k_B T \Delta V''_{\alpha_i,\alpha_f}(R_S)}{\hbar\mu}\right)^{1/3}. \tag{49}$$

Thus, in accordance with Eq. (26), in the presence of the external rotating electric field, the frequency $\omega^{\rm BC}_{\max}$ at which the maximum of the rainbow satellite peak occurs is

$$\omega^{\rm BC}_{\max} = \omega^C_{\max} + \Delta\omega^F_{\alpha_i,\alpha_f} + (\delta_{\alpha_f} - \delta_{\alpha_i}), \tag{50}$$

where

$$\omega^C_{\max} = \omega^C_S + 0.328\,814 \left(\frac{k_B T \Delta V''_{\alpha_i,\alpha_f}(R_S)}{\hbar\mu}\right)^{1/3} \tag{51}$$

is the frequency at which the maximum of this satellite is located in the absence of the rotating electric field, with ω^C_S the frequency of the rainbow singularity in the absence of the field as defined in Eq. (39). As follows from the above equations, the nonzero value of the difference $\omega^{\rm BC}_{\max} - \omega^C_{\max}$ may serve as an evidence for the appearance of the Berry phase effect in collisionally perturbed optical spectra.

2. *Effect of Berry phase on the red rainbow satellite of Lyman-α*

The classic example of a rainbow satellite is an absorption feature located at wavelength $\lambda_S = 162.3$ nm ($\omega_S = 2\pi c/\lambda_S = 1.161 \times 10^{16}$ rad s^{-1}) or at wave number $1/\lambda_S = 61\,610$ cm^{-1} in the red wing of the self-broadened Lyman-α line at wavelength $\lambda_0 = 121.6$ nm ($\omega_0 = 2\pi c/\lambda_0 = 1.549 \times 10^{16}$ rad s^{-1}) or at wave number $1/\lambda_S = 82\,230$ cm^{-1} of hydrogen [8]. This satellite can occur in absorption when two ground-state ($n = 1$) hydrogen atoms approach in the $X\,^1\Sigma_g^+$ state, absorb light, and undergo a transition to the $B\,^1\Sigma_u^+$ state corresponding to the resonance state ($n = 2$) of atomic H. Fully quantum-mechanical calculations of potential curves by Kołos and Wolniewicz [32] showed that the difference potential $\Delta V_{2,1}(R)$ for the $X\,^1\Sigma_g^+ - B\,^1\Sigma_u^+$ transitions has a minimum at $R_S = 4.1$ bohr, giving rise to a rainbow singularity at 162.3 nm. The shape of this satellite was the subject of several theoretical treatments starting from the pioneering work by Sando and Wormhoudt [28], followed by an extensive study due to Allard *et al.* [33]. However, the effect of Berry phase was not invoked in these papers.

The Stark effect caused by a rotating electric field on the Lyman-α line was first theoretically analyzed by Ishimura [34] and then by Lisitsa [35], but with no relation to the Berry-phase problem. On the other hand, Choi *et al.* [36] have presented a theoretical observation of Berry phase induced in excited hydrogenic atoms when they are placed in a slowly rotating uniform electric field whose direction may be adjusted adiabatically. Ishimura and Lisitsa have shown that in the general case (for arbitrary values ω_F of the rotating field frequency) the resonance level ($n = 2$) of hydrogen splits into nine sublevels. However, for small ω_F their treatments give four sublevels as in the case of a Stark effect by a static field. The case of static field corresponds to that in the rotating reference frame when the electric field is constant, and there are four Stark sublevels for $n = 2$. In terms of parabolic quantum numbers n_1 and n_2 these sublevels, designated as $\phi^{n_2-n_1,m}_{n=2}$, are as follows [37]: (1) $\phi_2^{-1,0} = (|200\rangle - |210\rangle)/\sqrt{2}$ with the Stark displacement $\Delta\omega_2^{-1,0}(F) = \Delta E_2^{-1,0}/\hbar = -3ea_0F/(Z\hbar)$, (2) $\phi_2^{1,0} = (|200\rangle + |210\rangle)/\sqrt{2}$ with the Stark displacement $\Delta\omega_2^{1,0}(F) = \Delta E_2^{1,0}/\hbar = 3ea_0F/(Z\hbar)$, and two sublevels with the zero

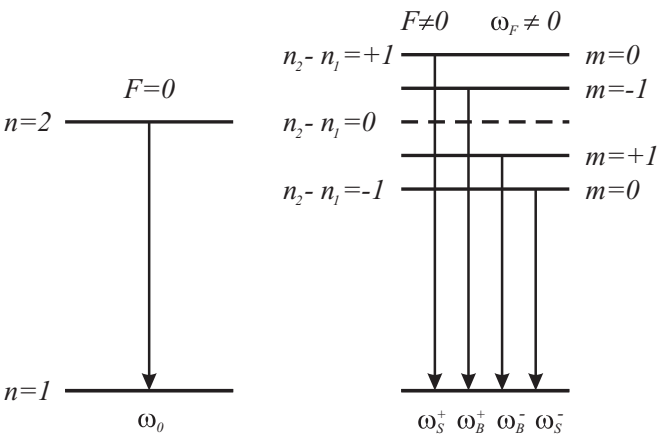

FIG. 1. Schematic diagram of the Stark and Berry phase effects on the Lyman-α line.

Stark displacement: (3) $\phi_2^{0,1} = |211\rangle$ with $\Delta E_2^{0,1} = 0$ and (4) $\phi_2^{0,-1} = |21-1\rangle$ with $\Delta E_2^{0,-1} = 0$.

The states $\phi_2^{-1,0}$, $\phi_2^{1,0}$, $\phi_2^{0,1}$, and $\phi_2^{0,-1}$ are chosen in the present work as the basis states. The ground state ($n = 1$) of the hydrogenlike atom is not affected by the external electric field. It is evident from Eqs. (12) and (13) that for the ground state of a hydrogenlike atom placed in an external rotating electric field, the Berry phase does not appear: $\gamma_1(t) = 0$. In the resonance state ($n = 2$), it can appear for the sublevels $\phi_2^{0,-1}$ and $\phi_2^{0,1}$ with $m = \pm 1$ and it becomes $\gamma_2^{0,-1}(t) = \Theta_F(t)$ and $\gamma_2^{0,1}(t) = -\Theta_F(t)$, respectively. For the sublevels $\phi_2^{\pm 1,0}$ corresponding to $m = 0$, the Berry phases vanish [$\gamma_2^{\pm 1,0}(t) = 0$]. Thus, in accordance with Eq. (14), for the sublevel $\phi_2^{0,-1}$ the Berry shift $\delta_2^{0,-1}$ amounts to $\delta = (1 - \cos\vartheta)\omega_F$, whereas for the sublevel $\phi_2^{0,1}$ it is $\delta_2^{0,1} = -\delta$. No Berry shift is expected for the sublevels $\phi_2^{1,0}$ and $\phi_2^{-1,0}$. The schematic diagram of the Stark and Berry phase effects on the Lyman-α line is shown in Fig. 1, where $\omega_S^{\pm} = \omega_0 \pm \Delta\omega(F)$, and $\omega_B^{\pm} = \omega_0 \pm \delta$.

In order to estimate the resultant profile $I_{2,1}^{\mathrm{BC}}(\omega)$ of the Lyman-α line, self-broadened by a gas placed in cone-rotating electric field, we use Eq. (46), in which the matrix elements of the spherical components er_0 and $er_{\pm 1}$ of the electric dipole moment are $\langle 100|er_0|210\rangle = eQ_{2,1}/\sqrt{3}$, $\langle 100|er_0|21 \pm 1\rangle = -eQ_{2,1}/\sqrt{3}$, and $\langle 100|er_0|200\rangle = \langle 100|er_-|21-1\rangle = \langle 100|er_+|211\rangle = 0$. Here $Q_{2,1}$ is the radial integral for the $2 \to 1$ transition in the hydrogenlike atom. The Wigner functions in Eq. (46) are $d_{00}^1(\vartheta) = \cos\vartheta$, and $d_{0-1}^1(\vartheta) = -d_{01}^1(\vartheta) = (\sqrt{2}/2)\sin\vartheta$. According to Eq. (22) the normalization factor now becomes $G = 1/6$. Substitution of these expressions into Eq. (46) yields [for $V_{\alpha_i}(R_C) \ll k_B T$]

$$I_{2,1}^{\mathrm{BC}}(\omega) = 24\hbar\pi(eQ_{2,1})^2 \times \left\{ \left[\frac{R_{+1,0}^2 |\pi z_{+1,0}|^{1/2}}{|\Delta V_{21}'(R_{+1,0})|} L(z_{+1,0}) + \frac{R_{-1,0}^2 |\pi z_{-1,0}|^{1/2}}{|\Delta V_{21}'(R_{-1,0})|} L(z_{-1,0}) \right] \cos^2\vartheta \right.$$
$$\left. + \left[\frac{R_{0,+1}^2 |\pi z_{0,+1}|^{1/2}}{|\Delta V_{21}'(R_{0,+1})|} L(z_{0,+1}) + \frac{R_{0,-1}^2 |\pi z_{0,-1}|^{1/2}}{|\Delta V_{21}'(R_{0,-1})|} L(z_{0,-1}) \right] \sin^2\vartheta \right\}. \quad (52)$$

Here the parameters $z_{\pm 1,0}$ and $z_{0,\pm 1}$ are given by Eq. (44), in which the Condon points $R_{\pm 1,0}$ and $R_{0,\pm 1}$, in accordance with Eq. (31), are solutions of

$$\hbar\xi_{\pm 1,0} = \Delta V_{2,1}(R_{\pm 1,0}), \quad (53)$$

and

$$\hbar\xi_{0,\pm 1} = \Delta V_{2,1}(R_{0,\pm 1}) \quad (54)$$

with

$$\xi_{\pm 1,0} = \omega - \omega_0 \pm \frac{3ea_0}{Z\hbar} F, \quad (55)$$

and

$$\xi_{0,\pm 1} = \omega - \omega_0 \pm \delta. \quad (56)$$

Let us note that in the absence of the external electric field ($F = 0$, $\omega_F = 0$), we have $\xi_{\pm 1,0} = \xi_{0,\pm 1} = \omega - \omega_0$ and $z_{\pm 1,0} = z_{0,\pm 1} = z_{\alpha_i,\alpha_f}$, where z_{α_i,α_f} is given by Eq. (44). Then Eqs. (53) and (54) become identical to Eq. (31) with $R_{\pm 1,0} = R_{0,\pm 1} = R_C^0$. In such a case Eq. (52) reduces to Eq. (43) which describes the intensity distribution in the wing of a single ($n = 2 \leftarrow n = 1$) pressure-broadened Lyman-α line.

3. *Lennard-Jones difference potential and its quadratic expansion*

To get more insight into the effect of Berry phase on the intensity distribution near rainbow satellites, we consider now a difference potential in the form of a Lennard-Jones (12-6) function:

$$\Delta V_{\alpha_i,\alpha_f}(R) = \hbar\varepsilon \left[\left(\frac{R_S}{R} \right)^{12} - 2 \left(\frac{R_S}{R} \right)^{6} \right], \quad (57)$$

where R_S is the position of the minimum, at which $\Delta V_{\alpha_i,\alpha_f}(R_S) = -\hbar\varepsilon$. The quasistatic rainbow singularity appears now on the red wing of a spectral line at the frequency displacement $\xi_{\alpha_i,\alpha_f}^S = -\varepsilon$. Following Ref. [8] we adopt for both real and complex Condon-point regions the quadratic approximation, Eq. (40), to the Lennard-Jones function about R_S. The result is

$$\Delta V_{\alpha_i,\alpha_f}(R) \approx -\hbar\varepsilon \left[1 - \frac{36}{R_S^2} (R - R_S)^2 \right]. \quad (58)$$

According to Eq. (30) for $\xi_{\alpha_i,\alpha_f} > -\varepsilon$, there are two real Condon points

$$R_C = R_S \pm \frac{R_S}{6} \left(\frac{\xi_{\alpha_i,\alpha_f}}{\varepsilon} + 1 \right)^{1/2}, \quad (59)$$

whereas for $\xi_{\alpha_i,\alpha_f} < -\varepsilon$ there is one pair of complex Condon points

$$R_C = R_S \pm i\frac{R_S}{6}\left(\left|\frac{\xi_{\alpha_i,\alpha_f}}{\varepsilon}\right| - 1\right)^{1/2}. \tag{60}$$

The parameter z_{α_i,α_f} can now be represented by

$$z_{\alpha_i,\alpha_f} = \left[\frac{\mu R_S^2}{72k_BT\varepsilon}\right]^{1/3}\left(\xi_{\alpha_i,\alpha_f} + \varepsilon\right), \tag{61}$$

in both quasistatic and antistatic regions. Thus, in accordance with Eqs. (21) and (43), in the limit $V_{\alpha_i}(R_C) \ll k_BT$, the resultant intensity distribution $I_{n_i,n_f}(\omega)$ in the rainbow satellite associated with red wing of the $n_i \to n_f$ spectral line of a hydrogenlike atom can be written

$$I^{\mathrm{BC}}_{n_i,n_f}(\omega) = \frac{2\pi R_C^2 R_S}{G\sqrt{\varepsilon}}\sum_{\alpha,m,m'}\left|d^1_{m,m'}\right|^2 \times \left|\langle\phi_{\alpha_i}|er_{m'}|\phi_{\alpha_f}\rangle\right|^2\frac{\left|z_{\alpha_i,\alpha_f}\pi\right|^{1/2}}{\left|\xi_{\alpha_i,\alpha_f}+\varepsilon\right|^{1/2}}L\left(z_{\alpha_i,\alpha_f}\right), \tag{62}$$

or equivalently

$$I^{\mathrm{BC}}_{n_i,n_f}(\omega) = \frac{2\pi^{3/2}R_C^2R_S}{G\sqrt{\varepsilon}}\left(\frac{\mu R_S^2}{72k_BT\varepsilon}\right)^{1/6} \times \sum_{\alpha_i,m,m'}\left|d^1_{m,m'}\right|^2\left|\langle\phi_{\alpha_i}|er_{m'}|\phi_{\alpha_f}\rangle\right|^2 L\left(z_{\alpha_i,\alpha_f}\right). \tag{63}$$

Since we are concerned here with the intensity distribution in the vicinity of the maximum of the rainbow satellite, we can assume that $R_C^2R_S \approx R_S^3$. This results from the fact that in the neighbourhood of the extremum of $\Delta V_{\alpha_i,\alpha_f}(R)$, the fitting of a quadratic function to the Lennard-Jones potential yields

$$R_C^2 = R_S^2\left[1 + \frac{1}{36}\left(1 + \frac{\xi_{\alpha_i,\alpha_f}}{\varepsilon}\right) \pm \frac{1}{3}\sqrt{1 + \frac{\xi_{\alpha_i,\alpha_f}}{\varepsilon}}\right]. \tag{64}$$

Making use of the appropriate expressions for $d^1_{m,m'}$ and $\langle\phi_{\alpha_i}|er_{m'}|\phi_{\alpha_f}\rangle$ for the $n = 2 \to n = 1$ transition, Eq. (62) can be transformed to

$$I^{\mathrm{BC}}_{2,1}(\omega) = B\{[L(z_{+1,0}) + L(z_{-1,0})]\cos^2\vartheta + [L(z_{0,+1}) + L(z_{0,-1})]\sin^2\vartheta\}, \tag{65}$$

where

$$B = (eQ_{2,1})\sqrt{\frac{\pi}{\varepsilon}}R_S^3\left(\frac{\mu R_S^2}{72k_BT\varepsilon}\right)^{1/6}. \tag{66}$$

Here,

$$z_{\pm1,0} = \left(\frac{\mu R_S^2}{72k_BT\varepsilon}\right)^{1/3}\left(\omega - \omega_0 \pm \frac{3ea_0}{Z\hbar}F + \varepsilon\right), \tag{67}$$

and

$$z_{0,\pm1} = \left(\frac{\mu R_S^2}{72k_BT\varepsilon}\right)^{1/3}(\omega - \omega_0 \pm \delta + \varepsilon). \tag{68}$$

As seen from Eq. (65), the shape of the rainbow satellite band observed in the presence of an external rotating electric field depends on the strength of the field as well as on the angle ϑ and on angular frequency ω_F of the field rotation. Using Eq. (64) we can correct for the fact that the Condon points do not actually occur at the extremum position R_S by multiplying the quantity B in Eq. (66) by a factor on the order of $[1 + (\xi_{\alpha_i,\alpha_f}/\varepsilon + 1)/36]$.

Let us note that in the absence of the external electric field ($F = 0, \omega_F = 0, \delta = 0$), we have $\xi_{\pm1,0} = \xi_{0,\pm1} = \omega - \omega_0$ and $z_{\pm1,0} = z_{0,\pm1} = z$, where now

$$z = \left(\frac{\mu R_S^2}{72k_BT\varepsilon}\right)^{1/3}(\omega - \omega_0 + \varepsilon). \tag{69}$$

Equation (65) becomes then

$$I^{\mathrm{BC}}_{2,1}(\omega) \to I^{C}_{2,1}(\omega) = 2BL(z) = 2(eQ_{2,1})\sqrt{\frac{\pi}{\varepsilon}}R_S^3\left(\frac{\mu R_S^2}{72k_BT\varepsilon}\right)^{1/6}L(z). \tag{70}$$

This formula describes the intensity distribution produced in the absence of the external rotating electric field. Its validity is restricted to the frequency region in the vicinity of the rainbow satellite maximum that corresponds to Condon points near the position R_S of the extremum in the difference potential.

As a measure of the magnitude of the effect caused on the rainbow satellite by Berry phase due to external rotating electric field, we can use the ratio $I^{\mathrm{BC}}_{2,1}(\omega)/I^{C}_{2,1}(\omega)$ which, in accordance with Eqs. (65) and (70), is

$$\frac{I^{\mathrm{BC}}_{2,1}(\omega)}{I^{C}_{2,1}(\omega)} = \frac{1}{2L(z)}\{[L(z_{+1,0}) + L(z_{-1,0})]\cos^2\vartheta + [L(z_{0,+1}) + L(z_{0,-1})]\sin^2\vartheta\}. \tag{71}$$

This means that a consequence of including Berry phase into the adiabatic quasimolecular wave functions is that the ratio of the intensity distribution observed in the presence of a rotating electric field to that observed in its absence should differ from one and be dependent on both the strength F of the field and the angular frequency ω_F of its rotation as well as on the angle ϑ.

V. SUMMARY AND DISCUSSION

We have added the effect of Berry phase to the formalism of adiabatic theories of pressure broadening to derive expressions for the shape of rainbow satellites accompanying the far wings of spectral lines emitted or absorbed by atoms placed in an external cone-rotating electric field. We found that the intensity distribution in far wings can be described in terms of the universal line shape function of the UFC theory provided the energy shifts due to Stark and Berry phase effects are incorporated as defined by Eq. (31). The basic result is the formula of Eq. (43), which shows that both the shapes and the positions of maxima of rainbow satellite bands associated with atomic lines radiated in the presence of a rotating electric field depend on frequency shifts caused by the Stark effect as well as the effects due to the Berry phase. The differences

between the data observed in the presence of a rotating field and those without that field provide a manifestation of the effects of Berry phase in pressure-broadened atomic spectra. As an example, we derived an expression for the shape of the rainbow satellite band located at 162.3 nm in the red wing of the self-broadened Lyman-α line of hydrogen, radiated in the presence of an external rotating electric field. It consists of four terms representing contributions to the intensity distribution coming from transitions between the ground state and corresponding Stark and Berry sublevels belonging to the resonance state. Approximate estimations made for a Lennard-Jones potential show that two quasistatic singularities induced by the Berry phase as determined from the condition $z_{0,\pm1} = 0$ [see Eq. (68)] are located symmetrically on both sides of the frequency $\omega_S^C = \omega_0 - \varepsilon$ of the singularity in the absence of the field. The first one is located in the short-wavelength region of the rainbow satellite at frequency $\omega_S^{\mathrm{BC}+} = \omega_S^C + \delta$, and the second one on the long-wavelength side at $\omega_S^{\mathrm{BC}-} = \omega_S^C - \delta$. In accordance with Eq. (71), the Berry shift depends on the angle ϑ and the angular frequency ω_F. In particular, for $\vartheta = 60^\circ$ this shift is $\delta = \omega_F/2$. The two remaining singularities are caused by the Stark shift and can be determined from the condition $z_{\pm1,0} = 0$. They are situated symmetrically on both sides of the frequency ω_S^C and are shifted from it by a factor $\Delta\omega(F) = \pm 3ea_0F/\hbar$.

The theory described in the present work requires the experimental verification. To this end a rotating electric field with high angular frequency ω_F (of the order of 10^{14} rad s^{-1}) sufficient to induce observable Berry and Stark effects is needed. However, such fields are not common, and their absence from experimental investigations explains the lack of experimental verification of the theoretical treatments of both the Stark effect on the Lyman-α line induced by rotating electric field, due to Ishimura [34] and Lisitsa [35], and the effect of Berry phase in hydrogenlike atoms placed in rotating field, calculated by Choi *et al.* [36]. Nevertheless, as Matveev and Musakhanov [1,2] have remarked, a cone-rotating field $\mathbf{F}$ of constant magnitude can be generated by superimposing a constant electric field $\mathbf{F}_1$ and the electric field $\mathbf{F}_2$ of a circularly polarized maser or laser, whose beam is aligned with $\mathbf{F}_1$. The resulting electric field $\mathbf{F} = \mathbf{F}_1 + \mathbf{F}_2$ is cone rotating with the angle $\vartheta = \tan^{-1}(F_2/F_1)$. To our knowledge, their proposal, which is equivalent to the application of the dynamic Stark effect for the case of a circularly polarized field, has not yet been realized experimentally, at least in the Berry phase context. It is noteworthy that Koryukina [38] performed a theoretical analysis of the shift and splitting of energy levels of rare-gas atoms caused by circularly polarized oscillating electric fields of strength up to 10 kV/cm and frequency of 100 MHz that can be generated in high-frequency electrodeless discharge lamps. However, the most promising way to produce cone-rotating electric field with the aim of its application to search the Berry phase effect on spectral line wings seems to be the use of various maser or laser light sources for circularly polarized radiation which are available at present (cf. e.g. [39]).

Of course the values of the strength F and angular frequency ω_F should be chosen so that the adiabatic criterion (18) is fulfilled. For the hydrogen Lyman-α line this criterion is $\omega_F < 6\pi a_0 eF/\hbar$. This means that for $\omega_F = 10^{14}$ rad/s, i.e., 1.59×10^{13} Hz, the electric field strength should be $F > F_{\mathrm{cr}} = 6.6 \times 10^5$ V/cm. Assuming that $F = 7 \times 10^5$ V/cm and using Eqs. (55) and (56), we obtain then for the angle $\vartheta = 75^\circ$ the values of the Berry shift $\delta = \pm 7.41 \times 10^{13}$ rad/s or $\delta = \pm 7.96 \times 10^{12}$ Hz or $\delta = \pm 393$ cm^{-1} and the Stark shift $\Delta\omega(F) = \pm 1.69 \times 10^{13}$ rad/s or $\pm 2.69 \times 10^{12}$ Hz or ± 89.7 cm^{-1}. Thus in this case the quasistatic singularities due to the Berry phase and Stark effect are located at ± 393.4 cm^{-1} and ± 89.7 cm^{-1}, respectively, on both sides of the classical rainbow singularity frequency ω_S^C corresponding to 61 610 cm^{-1}, i.e., 162.3 nm in wavelength scale. The critical strength value $F_{\mathrm{cr}} = 6.6 \times 10^5$ V/cm corresponds to a laser light intensity below 10^8 W/cm^2 for which nonlinear phenomena induced by the dynamic Stark effect, in particular multiphoton effects, are still negligible.

If we assume the angular frequency of the rotation of the external electric field to be $\omega_F = 10^{13}$ rad/s, i.e., 1.59×10^{12} Hz, which corresponds to the use of circularly polarized terahertz radiation, then the critical electric field strength value is $F_{\mathrm{cr}} = 6.6 \times 10^4$ V/cm. For $F = 7 \times 10^4$ V/cm and $\vartheta = 75^\circ$ we obtain from Eqs. (55)–(71) and (67),(68) the values of the Berry shift $\delta = \pm 7.41 \times 10^{12}$ rad/s or $\delta = \pm 39.3$ cm^{-1} and the Stark shift $\Delta\omega(F) = \pm 1.69 \times 10^{12}$ rad/s ± 8.97 cm^{-1}. This means that the additional intensity features induced by the Berry and Stark effects in this case are located near the maximum of the 162.3 nm rainbow satellite on both sides of it. Although these values of δ and $\Delta\omega(F)$ are small they can give rise to a marked modification of the resultant profile in comparison with that produced in the absence of an external field.

We should note that with an increase in the angular frequency ω_F, the critical value F_{cr} of the strength of rotating electric field as well as the Berry and Stark shifts increase. For instance, for $\omega_F = 10^{15}$ rad/s, we have $F_{\mathrm{cr}} = 6.6 \times 10^6$ V/cm. Assuming that $F = 7 \times 10^6$ V/cm and the angle $\vartheta = 75^\circ$ we get for the Berry shift the value ± 3930 cm^{-1} and for the Stark shift ± 897 cm^{-1}. However, this value of the electric field strength corresponds to an intensity of a laser radiation at which nonlinear phenomena due to the dynamic Stark effect may be important. Such large values of the critical electric field strength might appear to be the main obstacle in efforts to ascertain our theoretical results for the rainbow satellite at the Lyman-α line by experiment. On the other hand, it should be noted that the appearance of Berry phase can also be manifested as a modification of the Kuhn quasistatic distribution, Eqs. (34) and (35), in those cases where the difference potential function $\Delta V_{\alpha_i,\alpha_f}(R)$ has no extrema, i.e., when the rainbow satellites do not occur in the far wings. Such a modification can be observed for smaller values of the angular frequency ω_F and smaller values of critical electric field strength F_{cr} than those needed in experiments on rainbow satellites.

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