Does non-cyclic Berry phase play any role in the formation of pressure-broadened spectral line shapes?

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Abstract. The problem of the influence of contributions to the Berry phase coming from the motion of perturbers along open paths on the shapes of pressure-broadened spectral lines is examined by the use of the Born-Huang adiabatic approximation.

1. Introduction

In 1984 Berry [1] discovered that a state of a quantum system can acquire an extra phase of purely geometric origin when the system undergoes a cyclic adiabatic evolution, i.e. when it completes a closed path in parameter space. Recently, the concept of Berry’s geometric phase was included in the formalisms of adiabatic theories of pressure broadening to derive expressions for the intensity distribution both in the core [2] and far wings [3] of spectral lines radiated by atoms placed in an external electric field rotating around a cone about a fixed axis. In the limit of slow rotation on a closed path such that the electric field has constant magnitude but returns to its original position, the atomic levels suffer energy shifts due to a Berry phase in addition to those due to the interaction of the radiating atom with the perturbers. Results of analyses reported in Refs. [2] and [3] seem to indicate the importance of the effect caused by Berry’s phase on pressure-broadened spectral lines in cases when some parameters describing molecular system such as the external electric field traverse a closed path. Since the perturbers surrounding the radiating atom do not move along closed paths, the contributions to the Berry phase coming from the time dependence of the perturber coordinates \( \mathbf{R}(t) \) were assumed to be negligible in these analyses. It was shown, however, by several researches that the geometric phase makes sense also for non-cyclic adiabatic evolution, corresponding to open paths in...
parameter space [4-7]. Therefore, in the present work we address ourselves to the following problem: Should the phase contribution coming from open paths in $R$ space, i.e. those resulting from non-cyclic perturber motions, give rise to observable effects on intensity distribution in pressure-broadened spectral lines? We were stimulated by two papers by Zygelman [8, 9], in which he demonstrated the appearance of Berry’s phase in the context of atomic collision problems and suggested that this effect should be seen in spectral line shapes.

2. Berry vector gauge potentials

Let $\phi_{\alpha}(r,R)$ and $\phi_{\beta}(r,R)$ denote the electronic eigenfunctions of a diatomic quasimolecule consisting of a radiating atom in the initial ($\alpha$) and the final ($\beta$) state, respectively, which undergoes a collision with one perturber at time $t$ at the distance $R=R(t)$. The Berry phase $\gamma_{\alpha}(t)$ (or $\gamma_{\beta}(t)$), can be written as the line integral along the curve from $R(0)$ at $t = 0$ to $R(t)$:

$$\gamma_{\alpha}(t) = \int_{R(0)}^{R(t)} A_{\alpha}(R) dR,$$

where

$$A_{\alpha}(R) = i[\phi_{\alpha}^{*}(r,R)\nabla_{R}\phi_{\alpha}(r,R)],$$

is called now the Berry vector gauge potential for the state $\alpha$. Both $\phi_{\alpha}(r,R)$ and $\phi_{\beta}(r,R)$ depend on the electron coordinates $r$ and parametrically on $R$. For non-cyclic evolutions the Berry phases are traditionally assumed to be zero on the basis of the Born-Fock gauge transformation. However, it was pointed out in many papers that this choice of gauge is not always possible globally. This feature enables us to consider the possible influence of contributions to the geometric phase coming from open ended paths of the perturbers on the intensity distribution of pressure broadened spectral lines.

3. Appearance of Berry vector potentials in pressure-broadened spectral line shapes

In the adiabatic approximation the total wave function $\Psi_{\alpha;f}(r,R)$ for the initial electronic state $\alpha$ of the radiator is written as a product:

$$\Psi_{\alpha;f}(r,R) = \phi_{\alpha}(r,R) \chi_{\alpha;f}(R),$$

where $\chi_{\alpha;f}(R)$ is the “perturber” wave function that describes the translational motion of a single perturber in the force field of the radiator being in the $\alpha$-state. The index $i$ (or $f$) denotes all quantum numbers for the initial (or final) continuum states with energies $E_i$ (or $E_f$) of the relative motion of the single perturber. The intensity distribution in the $\alpha \rightarrow \beta$ line is obtained by calculating first the total electric dipole transition matrix element.
\[ T_{\alpha\beta}(\omega_f) = \left\langle \chi_{\alpha,d}(\mathbf{R}) \right| \mathbf{D}_{\alpha\beta}(\mathbf{R}) \left| \chi_{\beta,f}(\mathbf{R}) \right\rangle, \tag{4} \]

where

\[ \mathbf{D}_{\alpha\beta}(\mathbf{R}) = \int d^3 \mathbf{r} \, \phi_{\alpha}^*(\mathbf{r}, \mathbf{R}) \mu \phi_{\beta}(\mathbf{r}, \mathbf{R}) \tag{5} \]

is the electronic dipole transition moment of the radiating atom which depends on \( \mathbf{R} \), and \( \mu \) is the dipole moment operator.

As was indicated by Mead and Truhlar \[10\], the calculation of the wave function \( \chi_{\alpha,d}(\mathbf{R}) \) (or \( \chi_{\beta,f}(\mathbf{R}) \)) in the framework of the conventional Born-Oppenheimer (BO) approximation does not allow for any of the effects connected with the Berry vector potentials since no coupling between electronic and perturber motions is taken into account. For the same reason such effects do not appear in the conventional quantum-mechanical treatments of pressure broadening of spectral lines based on the BO approximation [11-14]. On the other hand, they showed that the Born-Huang version [15-17] of the adiabatic approximation gives rise to a natural manifestation of geometric phases.

Following Moody et al. [18] in the Born-Huang approximation the equation for the perturber wave function can be written in gauge-covariant form:

\[ \left\{ -\frac{\hbar^2}{2m} \left( \nabla \cdot \mathbf{A}_\alpha(\mathbf{R}) \right)^2 + W_{\alpha}(\mathbf{R}) - E_\alpha \right\} \chi_{\alpha,d}(\mathbf{R}) = 0, \tag{6} \]

where \( \mathbf{A}_\alpha(\mathbf{R}) \) is the Berry vector potential for the \( \alpha \) state given by Eq. (2). Here \( W_{\alpha}(\mathbf{R}) \) (or \( W_{\beta}(\mathbf{R}) \)) denotes the interatomic potential acting between a perturber and the radiator in the \( \alpha \) (or \( \beta \)) state. Hence, the appearance of the Berry phase effect on the spectral line shape may be demonstrated by substituting the solutions of Eq. (6), \( \chi_{\alpha,d}(\mathbf{R}) \) and \( \chi_{\beta,f}(\mathbf{R}) \), into Eq. (4). An important feature is that \( \mathbf{A}_\alpha(\mathbf{R}) \) and \( \mathbf{A}_\beta(\mathbf{R}) \) transform as the one-dimensional unitary group U(1) when we change our choice of phases for the electronic wave functions \( \phi_{\alpha}(\mathbf{r}, \mathbf{R}) \) and \( \phi_{\beta}(\mathbf{r}, \mathbf{R}) \). These functions are defined here in a coordinate system with quantization axis fixed along the radius \( \mathbf{R} \) between the radiating and perturbing atoms. In this molecule-fixed frame the molecular terms \( W_{\alpha}(\mathbf{R}) \) and \( W_{\beta}(\mathbf{R}) \) are characterized by their quantum number \( \Lambda \), the projection of the electronic orbital angular momentum \( \mathbf{L} \) along the interatomic axis \( \mathbf{R} \).

### 4. Line shapes not affected by Berry phases

Using spherical coordinates Zygelman [8] has shown that for the \( \Sigma \) states (\( \Lambda = 0 \)) of a diatomic molecule, the only non-vanishing term for the Berry vector potential is the radial component. In such a case the curl of this vector vanishes at all \( \mathbf{R} \), and the Berry vector potential can be eliminated by the Born-Fock transformation. This means that if both \( W_{\alpha}(\mathbf{R}) \) and \( W_{\beta}(\mathbf{R}) \) belong to the \( \Sigma \) states, the
Berry phase effects cannot occur on spectral line profiles associated with the $\Sigma \rightarrow \Sigma$ molecular transitions.

Let us note that the Franck-Condon principle is equivalent to the assumption that the perturbation of electronic wave functions $\psi_\alpha(r, R)$ and $\psi_\beta(r, R)$ is so weak that their parametric dependence on $R$ can be ignored so that the electronic transition moment in Eq. (5) $D_{\alpha\beta}(R)$ can be replaced by a constant. In such a case one obtains from Eq. (2) that the Berry vector potentials $A_\alpha(R)$ and $A_\beta(R)$ become approximately equal to zero. Hence, one can conclude that for strong allowed transitions the effects of Berry’s phase play – if any – a rather marginal role in pressure broadening of corresponding spectral lines.

5. Berry phases and shapes of forbidden spectral lines

The situation looks different, however, in cases where the perturbers disturb the electronic wave functions $\psi_\alpha(r, R)$ and $\psi_\beta(r, R)$ so strongly that the assumption of a constant transition moment ceases to be valid. An example for which this assumption fails completely is that of collision-induced radiation at wavelengths corresponding to dipole-forbidden transitions, for which the unperturbed dipole transition moment for an isolated radiator vanishes: $D_{\alpha\beta}(R(\infty)) = 0$. The collision-induced spectra associated with forbidden lines may appear because the transition moment $D_{\alpha\beta}(R)$, which is extremely small for isolated atoms, can become as large as for an allowed transition when the perturber is very close to the radiator. In such cases the parametric dependence of $\psi_\alpha(r, R)$ and $\psi_\beta(r, R)$ on the coordinates of perturbers plays a crucial role and may create Berry vector potentials $A_\alpha(R)$ and $A_\beta(R)$ that do not vanish. As a consequence the line shape calculated on the basis of the matrix elements $T_{\alpha\beta}(\omega_\eta)$ determined from Eq. (4) for the wave functions $\chi_{\alpha,f}(R)$ or $\chi_{\beta,f}(R)$ by the use of the Born-Huang approximation, Eq. (6), should differ from that evaluated on the basis of the conventional BO approximation. This means that the effect caused on spectral line shapes by the Berry vector potential can be expressed through the difference of intensity distributions corresponding to the Born-Huang and Born-Oppenheimer approximation.

In searching of these effects one can consider the application of the Born-Huang approximation to calculate the shapes of collision-induced spectra in the alkali-rare-gas and oxygen-rare-gas systems, which in the past were the subject of numerous experiments. Comparison of the experimental data with profiles calculated on the basis of the conventional BO approximation shows that in some cases, e.g. for the $5S \rightarrow 6S$ and $5S \rightarrow 4D$ transitions in Rb-Ar as well as $4S \rightarrow 3D$ transition in K-He systems [19], complete disagreement occurs. One can thus speculate whether the inclusion of the Berry vector potential into the line shape calculations by the use of the Born-Huang wave functions instead of conventional BO ones would improve the agreement for these systems. Obviously, in order to obtain reliable results, the reliable potential curves $W_\alpha(R)$ and $W_\beta(R)$ must be used in these calculations.
6. Conclusions

We have examined the possible implications of the Berry vector gauge potential for the pressure broadening of spectral lines, and found that this effect is negligible for strong allowed transitions. In general, the effect due to Berry potential does not play any role for spectral features associated with Σ – Σ transitions. On the other hand, the Berry potential effect is expected to have some importance for collision-induced spectra associated with dipole forbidden transitions.

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