

Tutorial/Article didactique

The evolution and revival structure of angular momentum quantum wave packets

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Abstract: In this paper, a coherent superposition of angular-momentum states created by absorption of polarized light by molecules is analyzed. Attention is paid to the time evolution of wave packets representing the spatial orientation of the internuclear axis of a diatomic molecule. Two examples are considered in detail. Molecules absorbing light in a permanent magnetic field experiencing the Zeeman effect and molecules absorbing light in a permanent electric field experiencing the quadratic Stark effect. In a magnetic field, we have a wave packet that evolves in time exactly as a classical dipole oscillator in a permanent magnetic field (classical-physics picture of the Zeeman effect). In the second case, we have a wave packet that goes through periodical changes of shape of the packet with revivals of the initial shape. This is pure quantum behavior. The classical motion of angular momentum in an electric field in the case of a quadratic Stark effect is known to be aperiodic. Solutions obtained for wave packet evolution are briefly compared with Rydberg-state coherent wave packets and harmonic-oscillator wave packets. Zeeman and Stark effects in small molecules continuously attract the attention of researchers, theoreticians, as well as experimentalists. These investigations allow us to obtain a deeper understanding of the interaction of molecules with stationary external fields and also can be used as a practical tool to measure different molecular characteristics, such as permanent electric or magnetic dipole moments, intramolecular perturbations, etc. It is worthwhile analyzing these effects as an evolution of wave packets. All this motivates a comparison of the quantum and classical picture of Zeeman and Stark effects in molecules.

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Résumé: Nous analysons une superposition cohérente d'états de moment angulaire créés par absorption de lumière polarisée par des molécules. Nous étudions particulièrement l'évolution du paquet d'onde représentant l'orientation spatiale de l'axe internucléaire de molécules diatomiques. Deux exemples sont étudiés avec plus d'attention : des molécules absorbant de la lumière en expérimentant un effet Zeeman dû à un champ magnétique externe et des molécules absorbant de la lumière en expérimentant un effet Stark dû à un champ électrique externe. Dans le champ magnétique, le paquet d'onde évolue dans le temps exactement comme un oscillateur dipolaire classique dans un champ magnétique permanent (vue classique de l'effet Zeeman). Dans le champ électrique, le paquet d'onde subit des changements de forme aperiodiques, avec retours à la forme initiale. Ce comportement est purement quantique. Nous savons que

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l'évolution du moment angulaire classique dans un champ électrique est apériodique. Des solutions obtenues pour l'évolution du paquet d'onde sont comparées à des paquets d'onde cohérents de Rydberg et à des paquets d'onde de l'oscillateur harmonique. Les effets Zeeman et Stark dans les petites molécules continuent d'attirer l'attention des chercheurs, aussi bien théoriciens qu'expérimentateurs. Ces études permettent de mieux comprendre l'interaction des molécules avec différents champs stationnaires externes et sont un outil pratique pour mesurer différentes caractéristiques moléculaires, tels les moments électrique et magnétique permanents, les perturbations intramoléculaires, etc. Il vaut la peine d'analyser ces effets via l'évolution de paquets d'onde. Tout cela justifie la comparaison des descriptions classique et quantique des effets Zeeman et Stark.

[Traduit par la rédaction]

1. Introduction

There are some problems that can be found in every classical-mechanics text book. For example, rotation of the planets around the Sun under the action of the gravitation force or the oscillations of a pendulum under the action of the quasielastic force.

In quantum mechanics there are very similar problems of the same importance. The motion of the electron around the nucleus under the action of the Coulomb force or the vibration of a diatomic molecule along the line connecting both nuclei. To compare these two sets of problems from which the first belongs to the macroscopic world and the other to the microscopic world one can ask questions of the type: Is it possible to observe the motion of an electron in a Kepler orbit around the nucleus in the same way as it is possible to observe the motion of the planet around the Sun? That is, is it possible to obtain experimentally a Rutherford atom when an electron rotates around the nucleus in a Kepler orbit? Is it possible to observe oscillations of the nuclei in a molecule that are similar to classical oscillations of a point particle bound by a quasielastic force? An affirmative answer to these questions, as is well known, is given by the correspondence principle of quantum mechanics [1].

The most common way to examine experimentally objects in the micro world is by their interaction with light. At the same time, it is common wisdom, see, for example ref. 1, that the methods of ordinary optical spectroscopy generally involve excitation of individual stationary states of atoms and molecules. Such states describe objects that are quantum mechanical by nature. For example, even for arbitrarily large quantum numbers a single stationary state of an electron in a Coulomb field does not come close to describing the motion of a localized particle in a Kepler orbit, just as for any quantum number, a stationary wave function of a harmonic oscillator does not describe the harmonic oscillations of a localized particle. In fact, classical motion is never obtained from excitation of a single quantum state.

Recently, with the use of ultrashort optical pulses, it has become possible to create coherent superpositions of many quantum states to obtain localized wave packets that are particlelike objects that obey quasiclassical laws, see refs. 2, 3 and references cited therein. Usually, electrons moving in orbits with large radii and oscillations of molecules are examined in these experiments. The processes with these wave packets usually are very fast — often occurring on a picosecond or even on a femtosecond time scale. These types of processes are most often analyzed to examine correspondence between the classical and quantum description of the objects in the microscopic world.

The interaction of particles with definite angular momentum with electric and magnetic fields provides a second, more accessible, but less exploited, way to examine the correspondence between the quantum and classical nature of the microscopic world. For example, from the view point of classical physics, the angular-momentum vector of a charged particle spinning in a magnetic field will precess around the field direction with the Larmor frequency [4]

$$\omega_L = \frac{g_J \mu_B B}{\hbar} \quad (1)$$

preserving the projection of the angular momentum on the direction of the field. Here g_J is a Lande factor, μ_B is the Bohr magneton, and B is the magnetic-field strength. The phenomenon of the precession

of angular momentum in an external magnetic field has been investigated for several decades and its history goes back to spin echoes in magnetic resonances, see for example ref. 5 and references cited therein.

To determine the behavior of a particle — atom or molecule — in an external magnetic field in quantum mechanics, one must deal with the particle's angular-momentum states and corresponding wave functions $Y_{JM}(\theta, \varphi)$. To obtain the classical-like motion of quantum angular momentum in an external field one must analyze the superposition of angular-momentum states. For diatomic molecules, the squared modulus of this superpositional wave packet $\Psi(\theta, \varphi, t)$ will show the probability of finding the molecular axis with a certain orientation in space. Namely, $|\Psi(\theta, \varphi, t)|^2 \sin\theta d\theta d\varphi$ is the probability of finding the molecular axis in the direction in space characterized by the spherical angles θ and φ . For the case of molecules, this approach has another advantage. To compare classical and quantum results usually one wants to examine the behavior of the system as the angular momentum becomes large. According to the correspondence principle the states with large angular momentum should behave classically. For the rotational states of molecules it is very common and straightforward to create states with large angular-momentum quantum numbers, with $J \sim 100$ being typical [6]. The situation is different for the case of atomic Rydberg states. It is not at all easy to create states with principal quantum number n close to 100 in a laboratory [2].

Partially, the problem of obtaining coherent superposition of angular-momentum states was solved many years ago, when quantum beats in an external magnetic field were observed experimentally for the first time by Aleksandrov in Russia [7] and by Dodd with co-workers in the United Kingdom [8]. They used light pulses to excite several angular-momentum states $|J, M\rangle = Y_{JM}(\theta, \varphi)$ with the same angular-momentum quantum number J , but different magnetic quantum numbers M simultaneously and coherently. In an external magnetic field these angular-momentum states have different energies E_M and hence the corresponding wave functions have different phase factors $\exp[-i(E_M/\hbar)t]$. In an experiment, one can observe the harmonic time dependencies of polarized fluorescence that correspond to the beats between these wave functions with different phase factors in the same way that in signal processing one can observe beats between two or more harmonic signals with slightly different frequencies.

From a practical view point, these experiments can be more straightforward than experiments with Rydberg-state atoms or instant excitation of oscillations in molecules. An obvious reason for this is that the speed of the processes in an external field usually are slower and, in any case, it can be controlled by controlling the external field strength. As a result, for the excitation of the state one can use much longer laser pulses and also observations of the state dynamics can be made by much slower experimental devices [6].

In this paper, quantum beat experiments will be analyzed by considering the creation and time evolution of angularly localized wave packets. This unique approach provides an opportunity to examine the correspondence between classical and quantum-mechanical periodic motion as induced by electric and magnetic fields. In our knowledge these experiments have not been analyzed before from these positions.

2. Revival structure of wave packets

The time-dependent wave functions for angularly localized angular-momentum quantum wave packets formed as a coherent superposition of angular-momentum eigenstates may be written as

$$\Psi(\theta, \varphi, t) = \sum_M c_M Y_{JM}(\theta, \varphi) \exp\left(-i \frac{E_M}{\hbar} t\right) \quad (2)$$

where $Y_{JM}(\theta, \varphi)$ is an ordinary spherical function [9] and the coefficients c_M are complex amplitudes.

We would like to examine to what extent and for how long time evolution of this wave packet coincides with the predictions of classical physics. For example, classically, an angular momentum of a

rotating rigid charge distribution will precess in a magnetic field with the Larmor frequency ω_L , see (1). If there is a coincidence between the quantum and classical description, then the position of the “center of gravity” of a spatially localized wave packet (the average value of the particle’s angular coordinates) must precess in space according to the rules of classical mechanics [4]

$$\frac{d\mathbf{J}}{dt} = \boldsymbol{\mu} \times \mathbf{B} \quad (3)$$

as is predicted by the Ehrenfest theorem [10, 11]. Here \mathbf{J} is a classical angular-momentum vector; $\boldsymbol{\mu}$, the magnetic dipole moment of particle; and \mathbf{B} , the strength of the external magnetic field.

The Ehrenfest theorem states that the quantum mean values of the quantities that characterize motion in quantum mechanics along with the mean values of the forces acting upon the particles are connected together exactly in the same way as the respective quantities are connected in classical physics. A detailed illustration of how the Ehrenfest theorem works in the case of angular-momentum precession in a magnetic field can be found in ref. 5.

Because classical particles have a definite direction of angular-momentum, wave packets localized in space usually have c_M well-centered around some particular mean quantum number \bar{M} . For a similar reason, wave packets that can be created from stationary atomic Rydberg-state wave functions are centered around some definite value \bar{n} of the principle quantum number n of the atomic state. Rydberg wave packets weighted by coefficients possessing Gaussian distribution [12] are particularly well investigated:

$$|c_n|^2 = \frac{1}{\sqrt{2\pi}\sigma} e^{-(n-\bar{n})/2\sigma^2} \quad (4)$$

Here the parameter σ characterizes the width of this distribution. Another particularly well-investigated case is the coherent states of a harmonic oscillator that can be obtained from harmonic oscillator wave functions $|v\rangle$ weighted by coefficients in the form [12]

$$c_v = e^{-(1/2)|\alpha|^2} \frac{\alpha^v}{\sqrt{v!}} \quad (5)$$

where v is the vibration quantum number and α is a parameter.

What we are interested in most, when we think about evolution of wave packets, is what are the laws governing the long-term postclassical evolution of wave packets beyond the bounds of the dynamics according to the correspondence principle?

The assumption that the weighting probabilities $|c_M|^2$ are strongly centered around a mean value \bar{M} (or \bar{n} , \bar{v}) means that only those states with energies E_M near the value $E_{\bar{M}}$ enter appreciably into the sum of (2). This permits an expansion of the energy in a Taylor series in M around the centrally excited value \bar{M}

$$E_M = E_{\bar{M}} + E'_{\bar{M}}(M - \bar{M}) + \frac{1}{2}E''_{\bar{M}}(M - \bar{M})^2 + \frac{1}{6}E'''_{\bar{M}}(M - \bar{M})^3 + \dots \quad (6)$$

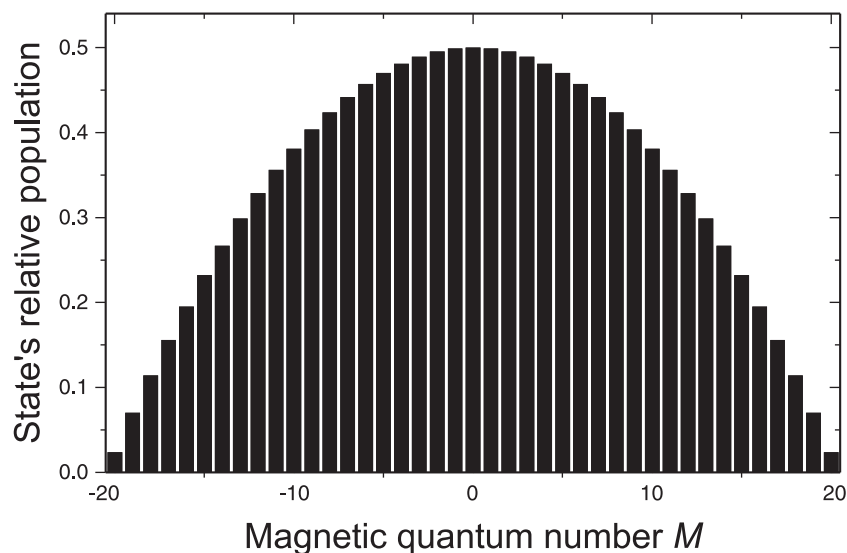
where each prime on $E_{\bar{M}}$ denotes a derivative at point $M = \bar{M}$.

The derivative terms in (6) define distinct time scales [1, 12]

$$T_{cl} = \frac{2\pi}{|E'_{\bar{M}}|}, \quad t_{rev} = \frac{2\pi}{\frac{1}{2}|E''_{\bar{M}}|}, \quad t_{sr} = \frac{2\pi}{\frac{1}{6}|E'''_{\bar{M}}|} \quad (7)$$

The first time scale, T_{cl} , is called the classical period. It is the period after which the system returns to its initial position according to the laws of classical physics. The second time scale, t_{rev} , is the revival time. This is a time after which the initial wave function will be partially or completely rebuilt. The third time

Fig. 1. Relative population distribution among magnetic substates $|J, M\rangle$ for an angular-momentum state with $J = 20$.



scale, t_{sr} , is the superrevival time. It represents the time after which the wave function will be rebuilt in case it is only partially rebuilt after the revival time. In practice almost always $T_{\text{cl}} \ll t_{\text{rev}} \ll t_{\text{sr}}$. Nevertheless, as we will see in the case of angular momentum in an electric field, this time scale order in a special situation can also be different.

The initial wave function is rebuilt each time the initial relations at $t = 0$ between the phases of the wave-function components $Y_{JM}(\theta, \varphi) \exp\left(-i\frac{E_M}{\hbar}t\right)$ in summation (2) are restored. The time behavior of the wave packet can easily be understood if we rewrite (2) with (6) keeping the terms through third order and disregarding the overall time-dependant phase [12]

$$\Psi(\theta, \varphi, t) = \sum_M c_M Y_{JM}(\theta, \varphi) \exp\left[-i2\pi\left(\frac{(M - \bar{M})t}{T_{\text{cl}}} + \frac{(M - \bar{M})^2 t}{t_{\text{rev}}} + \frac{(M - \bar{M})^3 t}{t_{\text{sr}}}\right)\right] \quad (8)$$

For small values of time t the first term in this equation dominates and the wave packet behavior is periodic with period T_{cl} . As time t increases a second term in an exponential factor starts to play a role and causes the wave packet to disperse. When time t approaches t_{rev} the second term in the exponential factor approaches 2π and then plays no further role. Periodic motion with period T_{cl} is restored again. The analysis can be continued and in the same manner the next term in the exponential factor of (8) can be analyzed. This governs the long time revival with characteristic time t_{sr} . At special times that are rational fractions of t_{rev} , the wave packet gathers into a series of subsidiary waves called fractional revivals [1].

One particularly good thing about the evolution of angular-momentum wave packets is that we can know *exactly*, and to some extent control, the c_M distribution that will occur in a realistic experiment by changing the excitation geometry and polarization of the excitation light.

As an example, let us consider a so called Q -type of molecular transition when light excites molecules from the ground state to the excited state and both states have the same value of angular-momentum quantum number J . Let us further assume that the exciting radiation is linearly polarized with the light electric-field vector \mathbf{F} lying perpendicularly to an external magnetic field \mathbf{B} . The probability of

finding molecules in a particular angular-momentum state $Y_{JM}(\theta, \varphi)$ can be found by determining the diagonal elements of the density matrix f_{MM} , which give the population of angular-momentum substates characterized by a magnetic quantum number M (for details see Appendix A and refs. 4 and 6)

$$\begin{aligned} f_{MM} &= |c_M|^2 = \sum_{\mu} |\langle M | \mathbf{F}^* \cdot \mathbf{d} | \mu \rangle|^2 \\ &= \frac{1}{2} \left[\left(C_{11JM-1}^{JM} \right)^2 + \left(C_{1-1JM+1}^{JM} \right)^2 \right] = \frac{1}{2} - \frac{M^2}{2J(J+1)} \end{aligned} \quad (9)$$

Here $\langle M | \mathbf{F}^* \cdot \mathbf{d} | \mu \rangle$ is the optical transition matrix element, \mathbf{d} is the optical transition dipole moment operator, C_{11JM-1}^{JM} is the Clebsch–Gordan coefficient [9], and μ is a ground-state magnetic quantum number. In this expression Clebsch–Gordan coefficients of the type C_{11JM-1}^{JM} represent the quantum-mechanical probability to excite an angular-momentum state $|J', M\rangle$ from an initial (usually ground) state $|J'', \mu = M - 1\rangle$. In this particular case of a Q -type molecular transition, the absorption of light does not change the angular momentum of the molecule or atom, so $J'' = J' = J$. As an example, for $J = 20$, $f_{MM} = |c_M|^2$ as calculated from (9) is given in Fig. 1.

Off-diagonal elements of the density matrix represent the coherence (phase relations) between different angular-momenta substates. Off-diagonal matrix elements can be calculated as

$$f_{MM'} = \overline{c_M c_{M'}^*} = \sum_{\mu} \langle M | \mathbf{F}^* \cdot \mathbf{d} | \mu \rangle \langle M' | \mathbf{F}^* \cdot \mathbf{d} | \mu \rangle^* \quad (10)$$

For Q -excitation with a pulsed light polarized along the y axis, besides the diagonal matrix elements calculated according to (9) we will have the following nonzero off-diagonal matrix elements [4]

$$f_{M+1, M-1} = f_{M-1, M+1} = \frac{1}{2} C_{JM-1}^{JM-1} C_{JM+1}^{JM+1} = -\frac{\sqrt{(J^2 - M^2) [(J+1)^2 - M^2]}}{4J(J+1)} \quad (11)$$

From the density-matrix elements for angular-momentum states, we can easily calculate the squared wave function that represents the probability density

$$|\Psi(\theta, \varphi, t)|^2 = \frac{3}{2J+1} \sum_{MM'} f_{MM'} Y_{JM} Y_{JM'}^* \exp(-i\omega_{MM'} t) \quad (12)$$

where $\omega_{MM'} = (E_M - E_{M'})/\hbar$.

3. Angular-momentum wave packets in a magnetic or an electric field

3.1. Atom or molecule in the external magnetic field

If an atom or molecule is in an external magnetic field experiencing the ordinary Zeeman effect, the angular-momentum state's J magnetic sublevels $|J, M\rangle$ with different magnetic quantum numbers M will have energies

$$E_M(M) = E^{(0)} + \frac{g_J \mu_B B M}{\hbar} = E^{(0)} + E_L M \quad (13)$$

where $E^{(0)}$ is the energy of a state in the absence of the external field. According to (7), we can expect classical period T_{cl} to be equal to $2\pi/E_L = 2\pi/(g_J \mu_B B/\hbar)$. All other periods will be infinite. Thus, the time evolution of this angular-momentum wave packet will be an infinitely long rotation around the external magnetic field direction with Larmor angular frequency $\omega_L = 2\pi/T_{cl}$. No changes apart from

the rotation in space around the magnetic-field direction will occur to the wave function. This is what actually has been observed experimentally in the past [13] as a harmonic modulation of an intensity of a polarized fluorescence from an ensemble of atoms or molecules excited by a short laser pulse. This is a well known effect of quantum beats induced by a magnetic field.

From the view point of an evolution of a wave packet, this result is similar to the well-known behavior for coherent states of a harmonic oscillator. In his pioneering paper, Ervin Schrödinger wrote as early as in 1926, that wave packets formed as coherent states of harmonic oscillator will oscillate infinitely long between classical turning points without dispersion, for references see ref. 12. The main reason for this is that the energies of quantum harmonic oscillator states depend *linearly* on the vibration quantum number v . It means that only the first derivative E'_v in the expansion of type (6) will differ from zero. In the case of the Zeeman effect, we observe the same linear energy dependence of the magnetic sublevels of atomic or molecular states on the magnetic quantum number M . As a result, according to (7), we have infinitely long classical-type motion of the wave packet that represents the precession of angular momentum in a magnetic field. One can easily calculate the angular-momentum distribution after the pulsed excitation following (10)–(12). This result appears to be independent of the value of the angular-momentum quantum number J . It is

$$|\Psi(\theta, \varphi, t)|^2 = \frac{3}{8\pi} \left[1 - \sin^2 \theta \sin^2(\varphi - \omega_L t) \right] \quad (14)$$

We have a donut-shaped wave function that rotates in space around the z axis with Larmor frequency ω_L , (1) [6], see Fig. 2. The fact that the result is independent of the angular-momentum quantum number J is worthy of mention. It is interesting especially because this distribution coincides precisely with the result that would appear if we considered absorption of the electric dipole oscillator in classical physics in the same circumstances. Indeed, if instead of considering artificial wave packets that can only be studied theoretically, we consider wave packets that can be obtained in a realistic experiment, it is not uncommon for quantum and classical results to coincide even for small quantum numbers, see ref. 6. In the classical approach, this donut-shaped distribution of the molecular axis can be understood if one keeps in mind that for Q -type molecular transitions the absorbing dipole is oriented along \mathbf{J} , that is, perpendicularly to the intermolecular axis of the rotating molecule [6].

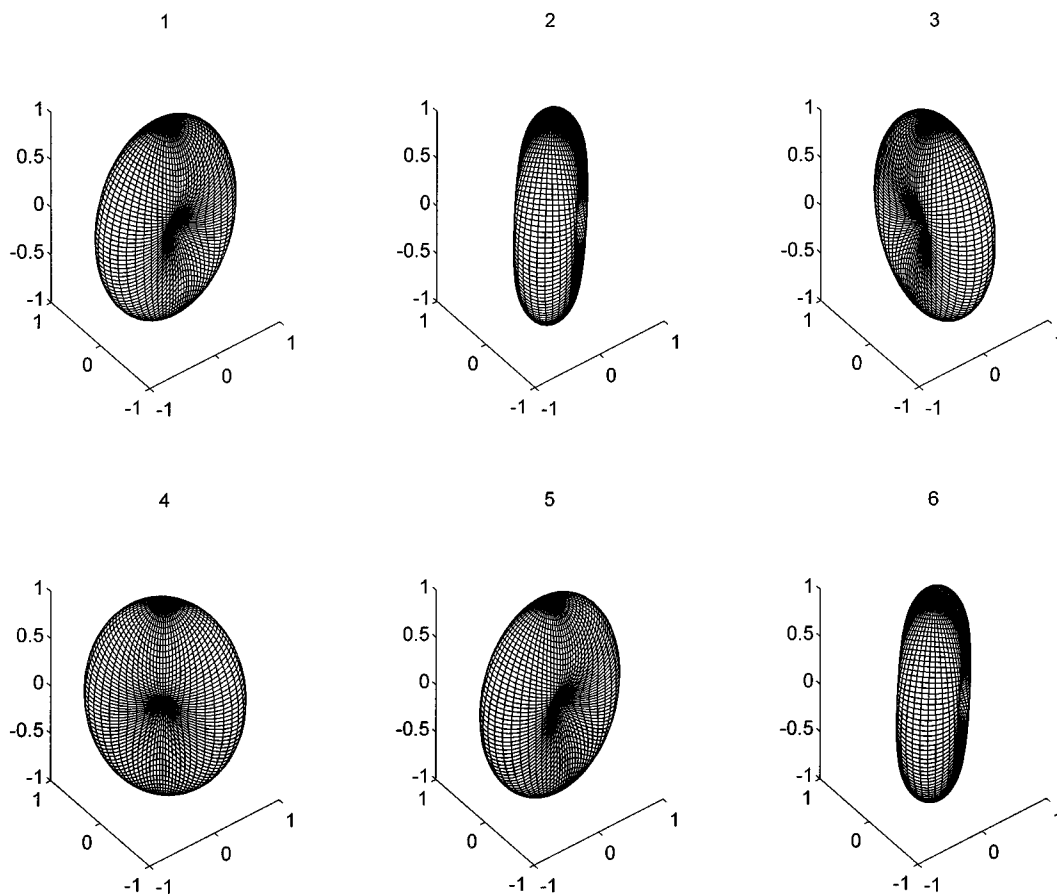
There are numerous examples when the Zeeman effect in molecules is observed experimentally. For a review see, for example, ref. 6. In these experiments pulsed optical excitation, leading to the distribution of the type described by (14), as well as continuous excitation was used. Typical precession frequencies for molecules in an excited state in these experiments was on the MHz scale (precession period $T \sim 10^{-6}$ s). It must be mentioned that to obtain this precession frequency in the case of molecules one must have a considerably stronger magnetic field than in the case of atoms. Typical magnetic-field strength in experiments with molecules is 0.01–0.1 T.

3.2. Molecule in an external electric field

The evolution of a molecular wave packet in an external electric field is quite distinct from the case of a magnetic field. For both cases we have the same amplitudes c_M of the partial components of the wave function in (2) and the same density matrix. But in case of an electric field we will have a different magnetic sublevel energy E_M dependence on the magnetic quantum number M . Let us consider a molecule in a state experiencing a quadratic Stark shift. This is the type of Stark effect most commonly observed with atoms and molecules. In this case, we will have an energy dependence on the magnetic quantum number of the form

$$E_M(M) = E^{(0)} + \frac{d^2 \mathcal{E}^2}{hB} \left[\frac{J(J+1) - 3M^2}{2J(J+1)(2J-1)(2J+3)} \right] = E^{(0)} + E_{\text{Stark}}^{(1)}(\mathcal{E}) + E_{\text{Stark}}^{(2)}(\mathcal{E})M^2 \quad (15)$$

Fig. 2. Wave-function evolution in an external magnetic field. 1 - $\omega_L t = 0$, 2 - $\omega_L t = \pi/4$, 3 - $\omega_L t = \pi/2$, 4 - $\omega_L t = 3/4\pi$, 5 - $\omega_L t = \pi$, 6 - $\omega_L t = 5\pi/4$.



We know that in the case of the Stark effect, the classical motion of the angular momentum in an external electric field is aperiodic [4, 14]. This is exactly what we see from (15). The first derivative of $E_{M=0}^L$ is zero and that means that T_{cl} is infinite. At the same time, the second derivative

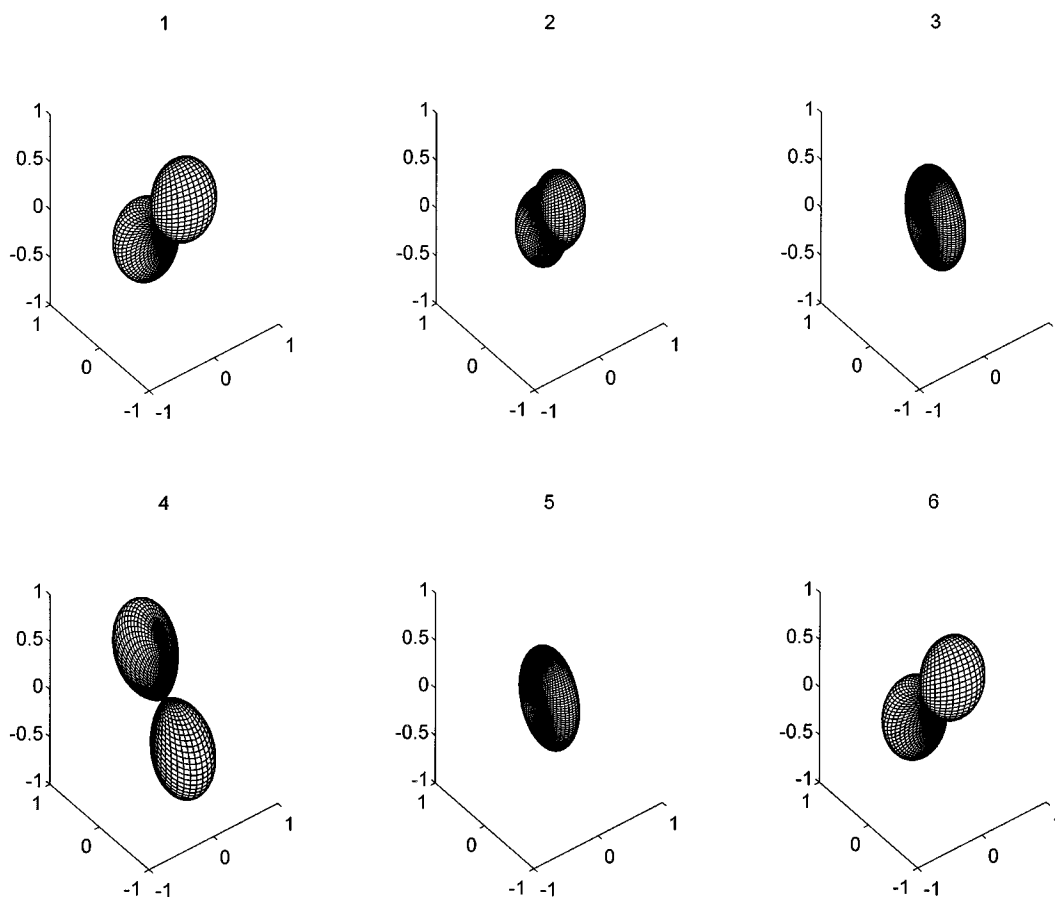
$$E_{M=0}^{L''} = - \left[\frac{3d^2 \mathcal{E}^2}{\hbar B J(J+1)(2J-1)(2J+3)} \right] \quad (16)$$

differs from zero and one can expect t_{rev} to be different from zero or infinity. This is exactly what was predicted for Stark quantum beats [15]. Figure 3 depicts one period of evolution of the wave function for state $J = 1$ excited by linearly polarized light with the \mathbf{F} vector lying in the zy plane and forming angle $\pi/4$ with the direction of an external electric field \mathcal{E} . R -type ($J = 0 \rightarrow J = 1$) optical transition is assumed. The analytical expression describing the probability density in Fig. 3 is

$$|\Psi(\theta, \varphi, t)|^2 = \frac{3}{8\pi} \left\{ 1 - \sin^2 \theta \cos^2 \varphi + \sin 2\theta \sin 2\varphi \cos[(2\pi/t_{rev})t] \right\} \quad (17)$$

It can be calculated using formulae (10), (12), and the Appendix.

Fig. 3. Stark quantum beats. $1 - t = 0$, $2 - t = \frac{1}{5}t_{\text{rev}}$, $3 - t = \frac{1}{4}t_{\text{rev}}$, $4 - t = \frac{1}{2}t_{\text{rev}}$, $5 - t = \frac{3}{4}t_{\text{rev}}$, $6 - t = t_{\text{rev}}$.



An interesting feature of the Stark effect is that the revival time

$$t_{\text{rev}} = \frac{4\pi h B J(J+1)(2J-1)(2J+3)}{3d^2 \mathcal{E}^2} \quad (18)$$

approaches infinity when the angular momentum approaches infinity, it means a particle with very large angular momentum starts to behave truly classically. This quantum-mechanical revival is not only as a peculiar behavior of wave function, but as well can be used to orient molecules in beams effectively [16]. From Fig. 3., it can be seen that after half of the revival time $t_{\text{rev}}/2$ the shape of the wave packet is fully restored only its orientation in space is changed by $\pi/2$. After the complete revival time t_{rev} , the wave function is restored fully in both shape and spatial orientation. It is worth mentioning, that although the electric-field intensity that is necessary to achieve easy observable revival time experimentally depends on the particular molecular constants and angular-momentum quantum number value, in some cases an extremely weak electric field of the order of 10 V/cm is sufficient. Probably other applications of the periodic behavior of atomic and molecular wave functions in electric fields can be foreseen.

In the last decade the Stark effect in diatomic molecules at stationary optical excitation was used rather extensively to determine different molecular properties, such as permanent and transition dipole moments, Lambda doubling constants, etc [17, 18].

4. Summary

This paper brings attention to and illustrates two examples of angular-momentum coherent wave packets that are of great interest owing to their peculiar properties. Less attention is paid to them than they deserve. These wave packets describe the precession of internuclear axes of diatomic molecules in an external field.

The first example was the angular-momentum coherent superposition state created by the absorption of polarized light by a molecule in an external magnetic field. There are many examples of such wave packets created in experiments for states of diatomic molecules [13]. But never has the situation of a coherent superposition of angular-momentum eigenstates been analyzed with the same machinery used to analyze the coherent superposition of Rydberg states or the coherent states of a harmonic oscillator. In experiments with molecules absorbing light in permanent external fields very often states with large rotational angular-momentum quantum numbers of $J \sim 100$ were involved. This allows us to compare these states with the behavior of a spinning particle in an external field.

It is known that classical angular momentum in an external magnetic field will precess around the magnetic-field direction with Larmor frequency ω_L .

A quantum wave packet in a magnetic field will experience the same motion. The period of rotation of the wave packet will coincide perfectly with the period of precession for classical angular momentum. The wave packet will last forever (actually as long as the excited state of molecule will live). It will not undergo any disintegration.

There is only one other example known when the wave packet evolves in time without dispersion. It is the coherent state of the harmonic oscillator [12]. The reason for this type of motion in both cases is the same. All coherently excited wave functions in these examples represent states that are equally separated on the energy scale, i.e., the systems have energy levels with equally separated steps.

Another example considered here was the angular-momentum states in an external electric field causing a quadratic Stark effect. In this case an ensemble of angular momentum will evolve aperiodically in classical physics [4]. In quantum physics, we will have periodical motion during which the wave function will periodically disintegrate and then, after a definite period, will go through a revival.

This is quite unique dynamics. It is more usual for systems to have a period of classical motion T_{cl} that is substantially shorter than the revival time t_{rev} , as is true for the Rydberg states or anharmonic oscillator states. It means that during one revival period this type of quantum system will undergo many classical periods. In the example of the quadratic Stark effect in an external electric field, we have exactly the opposite extreme. The system has no classical period at all. From the view point of classical physics the system is aperiodic. But quantum evolution of the wave function still has a well-defined period that becomes longer and longer, when angular moment of system increases and system approaches classical limit.

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Appendix A: Calculation of density matrix elements

Calculation of the density-matrix elements entering (9) and (10)

$$f_{MM'} = \sum_{\mu} \langle M | \mathbf{F}^* \cdot \mathbf{d} | \mu \rangle \langle M' | \mathbf{F}^* \cdot \mathbf{d} | \mu \rangle^* \quad (\text{A.1})$$

mainly consists in the calculation of quantum-mechanical matrix elements of a type

$$\langle M | \mathbf{F}^* \cdot \mathbf{d} | \mu \rangle \quad (\text{A.2})$$

Let us now have a look in more detail at how these matrix elements can be calculated. The first step is to calculate the *dot* or *scalar product* ($\mathbf{F}^* \cdot \mathbf{d}$) of the light electric-field vector \mathbf{F} and optical transition dipole moment \mathbf{d} . The meaning of this product is very close to that of a scalar or dot product of two ordinary vectors. Only in this case we are dealing with complex vectors and to find the projection of one vector onto another or — which is the same — to find “how much of one vector is contained in another” we must calculate this in a little bit more sophisticated a manner.

We are using here complex vectors, because it is a simple way to describe rotations in quantum mechanics as well as in classical physics. Let us see how these complex vectors and their components in a *cyclic system of coordinates* [6,9] can be used to describe, for example, the electric-field vector of light. Cyclic basis unit vectors are introduced according to the following rules

$$\begin{aligned} \mathbf{e}_{+1} &= -\frac{1}{\sqrt{2}}(\mathbf{e}_x + i\mathbf{e}_y) \\ \mathbf{e}_0 &= \mathbf{e}_z \\ \mathbf{e}_{-1} &= \frac{1}{\sqrt{2}}(\mathbf{e}_x - i\mathbf{e}_y) \end{aligned} \quad (\text{A.3})$$

where \mathbf{e}_x , \mathbf{e}_y , \mathbf{e}_z , are the basis unit vectors in Cartesian coordinates. If we now multiply these cyclic basis vectors by a phase factor $\exp(-i\Omega t)$ that represents some oscillations, for example, the oscillations of an electric field in a light wave, we can easily see, that for

$$\begin{aligned} \mathbf{e}_{+1}(-i\Omega t) &= -1/\sqrt{2}[\mathbf{e}_x \exp(-i\Omega t) + i\mathbf{e}_y \exp(-i\Omega t)] \\ &= -1/\sqrt{2}\{\mathbf{e}_x \exp(-i\Omega t) + \mathbf{e}_y \exp[-i(\Omega t - \pi/2)]\} \end{aligned} \quad (\text{A.4})$$

oscillations along the x axis are a quarter period ahead of those along the y axis and this means that this basis vector e_{+1} can be used to describe a left-handed circular polarized light beam, in the xy plane, that propagates in the positive direction of the z axis. It means a light wave in which the electric-field vector rotates counterclockwise if viewed in such a way that the radiation approaches the observer in the positive direction of the z axis.

In a similar way one can see that the e_{-1} basis vector represents a right-handed rotation and, in our particular case, can be used to describe right-handed circular polarized light that propagates along the z axis with the electric-field vector rotating in a clockwise direction in the xy plane.

Finally, the e_0 basis vector represents linear oscillations along the z axis and can be used to describe linearly polarized light when an electric field oscillates linearly along the z axis. Just as each vector can be represented by its three Cartesian components, each vector can be represented by its three cyclic components. In the case of the light polarization vector (and many other vectors in quantum mechanics) these cyclic components are more practical for calculation than the Cartesian representation.

The arbitrary electric-field vector \mathbf{F} in a light wave as well as any other vector may be resolved over cyclic unit vectors e_q

$$\mathbf{F} = \sum_q F^q e_q \quad (\text{A.5})$$

where the cyclic components F^q or the vector \mathbf{F} are connected to the Cartesian components of this vector as

$$\begin{aligned} F^{+1} &= -\frac{1}{\sqrt{2}}(F_x - iF_y) \\ F^0 &= F_z \\ F^{-1} &= \frac{1}{\sqrt{2}}(F_x + iF_y) \end{aligned} \quad (\text{A.6})$$

Now let us turn back to the matrix elements of a type (A.2). According to the vector algebra for cyclic vectors, the scalar product can be written as [6,9]

$$\langle M | \mathbf{F}^* \cdot \mathbf{d} | \mu \rangle = \sum_q (F^q)^* \langle M | d^q | \mu \rangle \quad (\text{A.7})$$

Further for a matrix element $\langle M | d^q | \mu \rangle$ we can apply the Wigner–Eckart theorem [6,9]. It allows us to separate the angular and dynamical part of this matrix element. What does this mean? For example, in classical physics if one wants to know how effectively an oscillating electric field \mathbf{F} can excite a linear dipole oscillator \mathbf{d} one must calculate the scalar product $(\mathbf{F} \cdot \mathbf{d}) = Fd \cos(\widehat{Fd})$. It means that we can separate the dynamic part Fd that describes the vector magnitude, and the angular part $\cos(\widehat{Fd})$ that represent their mutual orientation. In the same way in quantum physics the Wigner–Eckart theorem allows us to achieve the same separation for optical transition from the initial state $|J''\mu\rangle$ to excited state $|J'M\rangle$. Namely,

$$\langle M | d^q | \mu \rangle = \frac{1}{\sqrt{2J'+1}} C_{J''\mu 1q}^{J'M} \langle J' \| d \| J'' \rangle \quad (\text{A.8})$$

where $C_{J''\mu 1q}^{J'M}$ is a Clebsch–Gordan coefficient and $\langle J' \| d \| J'' \rangle$ is a reduced matrix element, that represents the dynamical part of the optical transition probability. It is obvious that the Clebsch–Gordan coefficient has a numerical value that depends on the values of the angular-momentum projections M and μ on the quantization axis z , and therefore it describes the angular-momentum orientation in space. This is the angular part of the transition probability.

If we now collect all these formulae together we can obtain the final expression that allows us to calculate easily matrix elements (A.1) for arbitrary light polarization and optical transition between arbitrary states

$$f_{MM'} = N \sum_{\mu q_1 q_2} (F^{q_1})^* (F^{q_2}) C_{J'' \mu 1 q_1}^{J' M} C_{J'' \mu 1 q_2}^{J' M'}. \quad (\text{A.9})$$

In this last expression a proportionality coefficient N that is insignificant for the purpose of this paper is not determined.