

Quantum defects and the long-term behavior of radial Rydberg wave packets

Robert Bluhm¹ and V. Alan Kostelecký²

¹Physics Department, Colby College, Waterville, Maine 04901

²Physics Department, Indiana University, Bloomington, Indiana 47405

(Received 1 July 1994; revised manuscript received 30 August 1994)

We show that a theoretical description of radial Rydberg wave packets in alkali-metal atoms based solely on hydrogenic wave functions and energies is insufficient to explain data that could be obtained in pump-probe experiments with current technology. The modifications to long-term revival times induced by quantum defects cannot be obtained by direct scaling of the hydrogenic results. Moreover, the effects of laser detuning and quantum defects are different. An alternative approach providing analytical predictions is presented.

PACS number(s): 32.80.-t, 03.65.Ge, 11.30.Pb

Radial Rydberg wave packets are produced when a short laser pulse excites a coherent superposition of states with no other fields present [1,2]. A single pulse produces a packet with p -state angular distribution but localized in the radial coordinate. Initially, the packet moves between the apsidal points of a classical Keplerian orbit. The radial-coordinate uncertainty product $\Delta r \Delta p$, correspondingly oscillates between values large compared to \hbar and values close to minimum uncertainty. Such oscillations are characteristic of a squeezed state. Indeed, a hydrogenic radial Rydberg wave packet at its first pass through the outer apsidal point may be modeled as a type of squeezed state, called a radial squeezed state [3]. The motion of a radial squeezed state undergoes a cycle involving collapse and fractional and full revivals characteristic of Rydberg wave packets [1,2,4–10].

Experiments on single-electron radial Rydberg wave packets typically involve alkali-metal atoms. It turns out that radial Rydberg packets in alkali-metal atoms can also be modeled using radial squeezed states [11]. In general, the core electrons of an alkali-metal atom cause deviations of the eigenenergies from hydrogenic values, which can be characterized by quantum defects $\delta(n, l)$ depending on the principal quantum number n and the angular-momentum quantum number l . For Rydberg states n is large and the $\delta(n, l)$ attain asymptotic values $\delta(l)$ independent of n . The energies in atomic units are then $E_{n^*} = -1/2n^{*2}$, where $n^* = n - \delta(l)$.

Recently, the revival structure of Rydberg wave packets both in hydrogen and in alkali-metal atoms has been studied for times much greater than the full revival time t_{rev} [12–14]. On a time scale $t_{\text{sr}} \gg t_{\text{rev}}$, a new cycle of fractional and full revivals commences. At times t_{frac} equal to linear combinations of t_{sr} and t_{rev} , the packet takes the form of a sum of macroscopically distinct subsidiary packets. In certain cases, only one subsidiary packet forms, more closely resembling the initial packet than the full-revival one. The motion of the packet at times near t_{frac} is periodic, with period T_{frac} given as a linear combination of the revival time t_{rev} and the classical orbital period T_{cl} . The autocorrelation function exhibits peaks near times t_{frac} with periodicities T_{frac} .

In this paper, we consider predictions for experimental results from different theoretical descriptions of the long-term evolution and revival structure of a radial Rydberg wave packet in an alkali-metal atom. In particular, we exam-

ine the suitability of an analysis of the long-term behavior based entirely on hydrogenic wave functions and energies, which is commonly used to describe such a wave packet. We show that this approach is inadequate for a complete description of phenomena accessible to the present generation of pump-probe experiments. For wave packets in alkali-metal atoms, where quantum defects are present, we also show that effects arising from laser detuning and from quantum defects are different.

For definiteness, we assume an experimental configuration with pump-probe detection involving either time-delayed photoionization [2] or phase modulation [15–17]. In either case, we take the packet to be produced by single-photon excitation from the ground state, yielding a p -state angular distribution. The superposition of eigenstates resulting from the initial laser pulse is characterized by a distribution c_{n^*} . The quantity $|c_{n^*}|^2$ describes the relative contributions of eigenstates with energies E_{n^*} . A short pulse produces a distribution of states with finite width centered on a value N^* , which need not correspond to an exact atomic resonance.

Both pump-probe methods produce an ionization signal displaying periodicities at the revival time. Reference [8] describes the observation of the photoionization signal for p -state radial wave packets in potassium with $N^* \approx 65.2$, for delay times up to $t \approx \frac{1}{2}t_{\text{rev}}$. The resolution of the data is sufficient to observe a relative phase shift approximately equal to $\frac{1}{2}T_{\text{cl}}$ between the initial peaks near $t \approx 0$ and the revival peaks near $t \approx \frac{1}{2}t_{\text{rev}}$. More recently, fractional revivals up to seventh order have been detected using the more sensitive phase-modulation technique [18]. These experiments, ranging over times up to $\frac{1}{2}t_{\text{rev}}$, resolve peaks in the ionization signal in rubidium with periods as small as $\frac{1}{7}T_{\text{cl}}$ for $N^* \approx 53.3$ and $\frac{1}{4}T_{\text{cl}}$ for $N^* \approx 46.5$.

For present purposes, we consider a hypothetical but feasible pump-probe experiment with a delay line such that the structure of the ionization signal can be examined at times on the order of t_{sr} . Although the time scale t_{sr} is greater than t_{rev} for the range of N^* values of interest [12], it is still several orders of magnitude smaller than the lifetimes of the Rydberg states. Since the periodicities in the peaks of the ionization signal match the periodicities of the underlying packet, a comparison of different theoretical models with each other and with experiment can be made by direct study of the wave packet.

In what follows, we take as experimental input to any given theory the measured values of the times t_{frac} at which periodicities appear in the ionization signal, the corresponding periods T_{frac} , and the central wavelength of the laser used to excite the packet. From the latter, the mean value of the energy E_{N^*} and hence $N^* = \sqrt{-1/2E_{N^*}}$ may be determined. This mean energy may not correspond to an atomic resonance.

The first model we consider involves hydrogenic eigenenergies and eigenstates. It is conceptually simple and is often used to study Rydberg packets. The wave function is expanded as

$$\Psi(\mathbf{r}, t) = \sum_{n=1}^{\infty} c_n \varphi_n(\mathbf{r}) \exp(-iE_n t), \quad (1)$$

where $\varphi_n(\mathbf{r})$ are p -state hydrogenic wave functions, $E_n = -1/2n^2$, and the distribution c_n has finite width and is centered around N^* . The superposition (1) therefore has mean energy matching that of the mean energy of the packet. *A priori*, this model might appear sufficient to describe the long-term evolution of a Rydberg wave packet in an alkali-metal atom. However, this is incorrect, as we demonstrate next.

The long-time revival structure of hydrogenic wave packets has already been studied for the case where the laser excites a mean energy corresponding to $N^* = \bar{N}$, where \bar{N} is an integer [12]. Using a Taylor expansion of the energy shows that the evolution of the packet for times up to a time t_{sr} is governed by the first three terms in the expansion. At present, we are interested in the general case with noninteger N^* . The desired results can be obtained from the earlier analysis by a judicious choice of variables. Let us write $N^* = \bar{N} - \mu/\nu$, where \bar{N} is the smallest integer greater than or equal to N^* and μ/ν is an irreducible fraction less than 1. In the present case of hydrogen, this fraction represents the laser detuning away from the nearby atomic resonance.

Expanding the hydrogenic energies to third order gives

$$E_n \approx E_{N^*} + E'_{N^*}(n - N^*) + \frac{1}{2}E''_{N^*}(n - N^*)^2 + \frac{1}{6}E'''_{N^*}(n - N^*)^3. \quad (2)$$

This expansion in powers of the noninteger quantity $(n - N^*)$ defines the time scales $T_{\text{cl}} = 2\pi N^{*3}$, $t_{\text{rev}} = \frac{2}{3}N^* T_{\text{cl}}$, and $t_{\text{sr}} = \frac{3}{4}N^* t_{\text{rev}}$. Introduce the integer quantity $k = (n - \bar{N})$ and define the new scales

$$T'_{\text{cl}} = T_{\text{cl}} \left(1 - \frac{2\mu}{\nu} \frac{T_{\text{cl}}}{t_{\text{rev}}} + \frac{3\mu^2}{\nu^2} \frac{T_{\text{cl}}}{t_{\text{sr}}} \right)^{-1}, \quad (3)$$

$$t'_{\text{rev}} = t_{\text{rev}} \left(1 - \frac{3\mu}{\nu} \frac{t_{\text{rev}}}{t_{\text{sr}}} \right)^{-1}, \quad (4)$$

$$t'_{\text{sr}} = t_{\text{sr}}, \quad (5)$$

in terms of which $\Psi(\mathbf{r}, t)$ may be written in the form

$$\Psi(\mathbf{r}, t) = \sum_{k=-\infty}^{\infty} c_k \varphi_k(\mathbf{r}) \exp \left[-2\pi i \left(\frac{kt}{T'_{\text{cl}}} - \frac{k^2 t}{t'_{\text{rev}}} + \frac{k^3 t}{t'_{\text{sr}}} \right) \right]. \quad (6)$$

Since by assumption $\bar{N} \gg 1$, the lower limit in k is well approximated by $-\infty$. An overall complex phase has been dropped.

With these variable changes, the wave function in Eq. (6) has a structure similar to that used in the earlier analysis with integer N^* . However, the three key time scales are modified by amounts depending on the laser detuning in hydrogen, i.e., the irreducible fraction μ/ν . Following the approach of Ref. [12], we can obtain the times of formation t'_{frac} of the subsidiary wave packets and their periodicities T'_{frac} . Write $\bar{N} = 4\eta + \lambda$, where η and λ are integers and $\lambda = 0, 1, 2, \text{ or } 3$. We then find

$$t'_{\text{frac}} = \frac{1}{q} t'_{\text{sr}} - \frac{m}{n} t'_{\text{rev}}, \quad T'_{\text{frac}} = \frac{3}{q} t'_{\text{rev}} - \frac{u}{v} T'_{\text{cl}}, \quad (7)$$

where q is an integer multiple of 3 and

$$\begin{aligned} \frac{m}{n} &= \frac{3}{4q} \left(\lambda - 5\frac{\mu}{\nu} \right) \pmod{1}, \\ \frac{u}{v} &= \frac{2(\eta + \lambda) - 3}{q} \pmod{1}. \end{aligned} \quad (8)$$

As expected, when $\mu \rightarrow 0$ the expressions reduce to those of Ref. [12], corresponding to excitation on resonance.

These results show that, using a hydrogenic expansion, the time t'_{frac} and T'_{frac} are completely determined once N^* has been fixed. However, this determination has come before specifying the alkali-metal atom in question, whereas quantum defects are known to cause additional shifts in the revival times [13]. We have therefore shown that describing a wave packet in an alkali-metal atom purely with hydrogenic energies and wave functions is insufficient for a complete treatment.

We next turn to a differential theoretical description that does provide a more complete description and therefore also permits an estimate of the deviations from hydrogenic behavior. Moreover, it allows a quantitative comparison of the effects of laser detuning and quantum defects.

Nonhydrogenic features of radial packets in alkali-metal atoms can be incorporated analytically via a supersymmetry-based quantum-defect theory (SQDT), which has analytical wave functions with the asymptotic Rydberg series as exact energy eigenvalues [19,20]. Since the SQDT wave functions $\varphi_{n^*}^*(\mathbf{r})$ both incorporate quantum defects and form a complete and orthonormal set, they can be used as a basis for an expansion of a packet in an alkali-metal atom. We write

$$\Psi(\mathbf{r}, t) = \sum_{n^*} c_{n^*} \varphi_{n^*}^*(\mathbf{r}) \exp(-iE_{n^*} t), \quad (9)$$

where c_{n^*} is a distribution in n^* centered on N^* .

Expanding the energy E_{n^*} as before around $N^* = \bar{N} - \mu/\nu$ defines the same three time scales as for the hydrogenic expansion: $T_{\text{cl}} = 2\pi N^{*3}$, $t_{\text{rev}} = \frac{2}{3}N^* T_{\text{cl}}$, and $t_{\text{sr}} = \frac{3}{4}N^* t_{\text{rev}}$. However, in this case the expansion is in powers of $(n^* - N^*) \equiv (k + \alpha/\beta)$, where we have introduced $\alpha/\beta = \mu/\nu - \delta(l) \pmod{1}$, and k is the integer part of $(n^* - N^*)$. For excitation in alkali-metal atoms, the laser

detuning from the nearby atomic resonance is α/β . Excitation on resonance corresponds to $\alpha=0$. The quantity μ/ν , which for the above analysis in hydrogen represented the laser detuning, is now instead the fractional part of the sum of the laser detuning and the quantum defect.

Keeping the first three terms in the energy expansion gives

$$\Psi(\mathbf{r}, t) = \sum_{k=-\infty}^{\infty} c_k \varphi_{*k}(\mathbf{r}) \exp \left[-2\pi i \left(\frac{kt}{T_{\text{cl}}^{*'}} - \frac{k^2 t}{t_{\text{rev}}^{*'}} + \frac{k^3 t}{t_{\text{sr}}^{*'}} \right) \right], \quad (10)$$

where

$$T_{\text{cl}}^{*'} = T_{\text{cl}} \left(1 - \frac{2\alpha}{\beta} \frac{T_{\text{cl}}}{t_{\text{rev}}} + \frac{3\alpha^2}{\beta^2} \frac{T_{\text{cl}}}{t_{\text{sr}}} \right)^{-1}, \quad (11)$$

$$t_{\text{rev}}^{*'} = t_{\text{rev}} \left(1 - \frac{3\alpha}{\beta} \frac{t_{\text{rev}}}{t_{\text{sr}}} \right)^{-1}, \quad (12)$$

$$t_{\text{sr}}^{*'} = t_{\text{sr}}. \quad (13)$$

It is important to note that these expressions depend on both the quantum defect δ and the laser detuning α/β . Part of the dependence on α/β is explicit. The remainder and the dependence on δ appear through the hidden dependence on the irreducible fraction μ/ν , which enters through the definitions of the time scales in terms of N^* .

Following the analysis in Ref. [13] with $\bar{N}=4\eta+\lambda$ as before, we find that the packet may be written as a sum of distinct subsidiary waves at times $t_{\text{frac}}^{*'}$, with periodicities $T_{\text{frac}}^{*'}$ given by

$$t_{\text{frac}}^{*'} = \frac{1}{q} t_{\text{sr}}^{*' } - \frac{m}{n} t_{\text{rev}}^{*' }, \quad T_{\text{frac}}^{*' } = \frac{3}{q} t_{\text{rev}}^{*' } - \frac{u}{v} T_{\text{cl}}^{*' }, \quad (14)$$

where

$$\frac{m}{n} = \frac{3}{4q} \left(\lambda - \frac{\mu}{\nu} - \frac{4\alpha}{\beta} \right) \pmod{1}, \quad (15)$$

$$\frac{u}{v} = \frac{2(\eta+\lambda)-3}{q} + \frac{2}{q} \left(\frac{\alpha}{\beta} - \frac{\mu}{\nu} \right) \pmod{1}.$$

The revival times and periodicities depend on the quantum defects. Unlike in hydrogen, specifying N^* fails to determine $t_{\text{frac}}^{*'}$ and $T_{\text{frac}}^{*'}$. In addition, the alkali-metal atom and the corresponding quantum defects must be specified. Moreover, the scales $t_{\text{frac}}^{*'}$ and $T_{\text{frac}}^{*'}$ in the present case evidently cannot be obtained from the corresponding hydrogenic scales t_{frac}' and T_{frac}' by a simple renormalization.

Equation (15) also demonstrates that the effects of quantum defects are different from those of the laser detuning. Replacing μ/ν with its definition in terms of the laser detuning α/β and the quantum defect δ shows that the time $t_{\text{frac}}^{*'}$ and the period $T_{\text{frac}}^{*'}$ have different dependences on δ and α/β . Therefore, laser detuning cannot be mimicked by quantum defects or vice versa. The differences arise because a constant shift in the laser detuning is equivalent to a constant (opposite) shift for all energy levels, whereas a constant shift

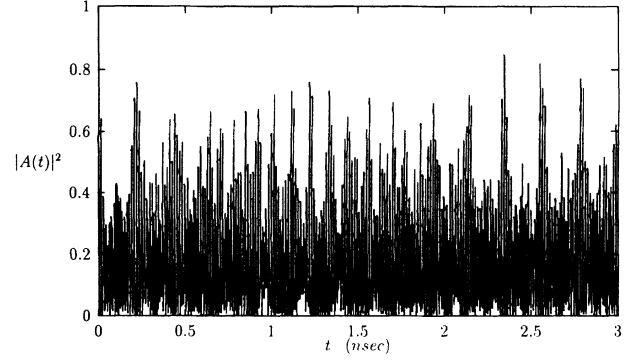


FIG. 1. Absolute square of the autocorrelation function for rubidium radial squeezed states with $N^* \approx 45.35$ as a function of time in nanoseconds.

in the quantum defect would correspond to varying shifts among the energy levels since $E_{n^*} = -1/2n^{*2}$. Furthermore, these differences are of the order of $t_{\text{rev}}^{*'}$, representing many classical orbital periods.

Next, we consider whether the modifications of the long-time revival behavior are experimentally observable with current technology. For simplicity in what follows, we take an example for which the excitation is at resonance. Consider a wave packet in rubidium with $N^* \approx 45.35$, which is of the type that can readily be produced experimentally. For definiteness set $q=6$, which would produce a large peak in the ionization signal in a pump-probe experiment as it corresponds to the formation of a single packet, more closely resembling the initial packet than does the original full revival. We then find that $\bar{N}=46$, $\eta=11$, $\lambda=2$, $\mu=13$, and $\nu=20$. The description of long-term revivals using hydrogenic energies and wave functions yields $t_{\text{frac}}' \approx 2.05$ nsec, with a periodicity $T_{\text{frac}}' \approx 215$ psec. In contrast, the description incorporating quantum defects also requires a specification of the quantum defect $\delta(1)$ for p states of rubidium, which we take to be $\delta(1) \approx 2.65$. This gives $\alpha/\beta=0$ and $t_{\text{frac}}^{*' } \approx 2.36$ nsec, with periodicity $T_{\text{frac}}^{*' } \approx 206$ psec.

This analysis shows that there is a difference of approximately 0.31 nsec between the predicted times for the occurrence of the $q=6$ long-term revival. This is greater than 20 classical orbital periods. A discrepancy of this size should be measurable in a pump-probe experiment with a delay line of approximately 2.5 nsec.

Additional support for the above analysis comes from the numerical computation of $t_{\text{frac}}^{*'}$ and $T_{\text{frac}}^{*'}$. The initial packet is taken as a p -state radial squeezed state for rubidium, with mean energy and mean radius at the outer apsidal point determined by the value $N^* \approx 45.35$. We numerically evolve this packet using the time-dependent Schrödinger radial equation with the SQDT effective potential.

Figure 1 shows the absolute square of the autocorrelation function for the radial squeezed states for times up to 3 nsec. For this case, $t_{\text{rev}} \approx 0.43$ nsec. The fractional revivals at $t \approx 0.07, 0.11, \text{ and } 0.22$ nsec agree with the predicted values $\frac{1}{6}t_{\text{rev}}$, $\frac{1}{4}t_{\text{rev}}$, and $\frac{1}{2}t_{\text{rev}}$, respectively. The peaks in the autocorrelation function at the full revival time t_{rev} are diminished relative to those at $\frac{1}{2}t_{\text{rev}}$, due to distortions of the packet arising from the higher-order terms in the energy expansion. Long-term revivals with $q=12, 9, \text{ and } 6$ are visible at times

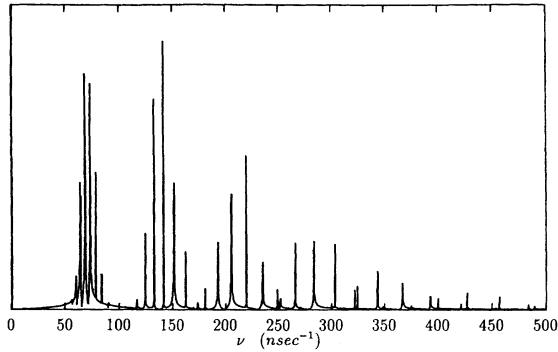


FIG. 2. Fourier spectrum for the absolute square of the autocorrelation function of rubidium radial squeezed states with $N^* \approx 45.35$. The unnormalized Fourier transform is plotted as a function of frequency in inverse nanoseconds.

in good agreement with the predictions $t_{\text{frac}}^{*'} \approx 1.17, 1.57,$ and 2.36 nsec, respectively. Furthermore, the peaks have periods agreeing with the predicted values $T_{\text{frac}}^{*'} \approx 0.10, 0.14,$ and 0.21 nsec for $q=12, 9,$ and 6 .

Figure 2 displays the Fourier transform of the numerical data for the autocorrelation function shown in Fig. 1. The dominant frequencies agree with those obtained from the energy spacings, $\nu = \Delta E_{n^*}/2\pi$, with $E_{n^*} = -1/2n^{*2}$. The beating of these frequencies leads to the revival structure observed in Fig. 1. This confirms that the Schrödinger equation with the SQDT effective potential generates the correct eigenenergies for an alkali-metal atom.

Analytically, we find $\Delta r \Delta p_r \approx 0.503$ for the packet at the outer apsidal point. The uncertainty product then oscillates as a function of time. Near $t_{\text{frac}}^{*'}$ with $q=6$, $\Delta r \Delta p_r$ is less than its value near t_{rev} , indicating that the $q=6$ long-term revival is closer to minimum uncertainty than the full revival. Figure

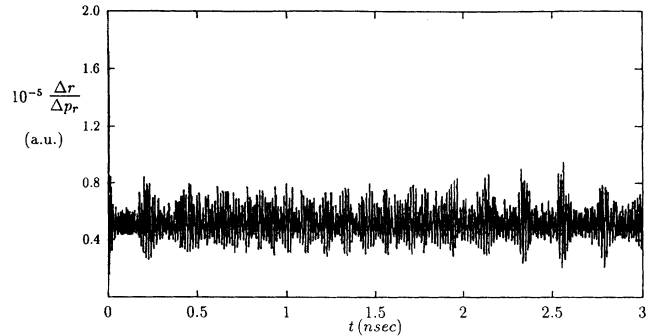


FIG. 3. The ratio of uncertainties $\Delta r/\Delta p_r$ in units of 10^5 a.u. as a function of time in nanoseconds for a radial squeezed state of rubidium with $N^* \approx 45.35$.

3 shows the uncertainty ratio $\Delta r/\Delta p_r$ as a function of time. The squeezing of the wave packet is visibly more extreme near the $q=6$ long-term revival at $t \approx 2.36$ nsec than at the full revival near $t \approx 0.43$ nsec. The uncertainty ratio oscillates around a mean value close to 50 000 in atomic units. This agrees with the value of $\Delta r/\Delta p_r$, calculated analytically in SQDT for an energy eigenstate with $n^* \approx 45.35$. Evidently, the long-term uncertainty ratio takes this mean value.

The analytical and numerical results we have presented in this work show that modifications of the hydrogenic long-term revival structure arise at an experimentally observable level for radial Rydberg wave packets in alkali-metal atoms. A description purely in terms of hydrogenic wave functions and energies is insufficient for an accurate prediction of the revival times and periodicities. Moreover, the effects of laser detuning and the quantum defects are different. An analytical treatment is possible within the context of SQDT. The predicted values of $t_{\text{frac}}^{*'}$ and $T_{\text{frac}}^{*'}$ for rubidium agree with those observed in the long-term behavior of a radial squeezed state.

-
- [1] J. Parker and C. R. Stroud, *Phys. Rev. Lett.* **56**, 716 (1986); *Phys. Scr.* **T12**, 70 (1986).
- [2] G. Alber, H. Ritsch, and P. Zoller, *Phys. Rev. A* **34**, 1058 (1986); G. Alber and P. Zoller, *Phys. Rep.* **199**, 231 (1991).
- [3] R. Bluhm and V. A. Kostecký, *Phys. Rev. A* **48**, 4047 (1993).
- [4] I. Sh. Averbukh and N. F. Perelman, *Phys. Lett.* **139A**, 449 (1989).
- [5] M. Nauenberg, *J. Phys. B* **23**, L385 (1990).
- [6] A. ten Wolde, L. D. Noordam, A. Lagendijk, and H. B. van Linden van den Heuvell, *Phys. Rev. Lett.* **61**, 2099 (1988).
- [7] J. A. Yeazell, M. Mallalieu, J. Parker, and C. R. Stroud, *Phys. Rev. A* **40**, 5040 (1989).
- [8] J. A. Yeazell, M. Mallalieu, and C. R. Stroud, *Phys. Rev. Lett.* **64**, 2007 (1990).
- [9] J. A. Yeazell and C. R. Stroud, *Phys. Rev. A* **43**, 5153 (1991).
- [10] D. R. Meacher, P. E. Meyler, I. G. Hughes, and P. Ewart, *J. Phys. B* **24**, L63 (1991).
- [11] R. Bluhm and V. A. Kostecký, *Phys. Rev. A* **49**, 4628 (1994).
- [12] R. Bluhm and V. A. Kostecký, Indiana University Report No. IUHET 275, 1994 (unpublished).
- [13] R. Bluhm and V. A. Kostecký, Indiana University Report No. IUHET 277, 1994 (unpublished).
- [14] Note that Ref. [1] also presents a long-term revival in hydrogen at $t = \bar{n}^3 T_{\text{cl}}$.
- [15] L. D. Noordam, D. I. Duncan, and T. F. Gallagher, *Phys. Rev. A* **45**, 4735 (1992).
- [16] B. Broers, J. F. Christian, J. H. Hoogenraad, W. J. van der Zande, H. B. van Linden van den Heuvell, and L. D. Noordam, *Phys. Rev. Lett.* **71**, 344 (1993).
- [17] J. F. Christian, B. Broers, J. H. Hoogenraad, W. J. van der Zande, and L. D. Noordam, *Opt. Commun.* **103**, 79 (1993).
- [18] J. Wals, H. H. Fielding, J. F. Christian, L. C. Snoek, W. J. van der Zande, and H. B. van Linden van den Heuvell, *Phys. Rev. Lett.* **72**, 3783 (1994).
- [19] V. A. Kostecký and M. M. Nieto, *Phys. Rev. A* **32**, 3243 (1985).
- [20] For a review of SQDT, see, for example, V. A. Kostecký, in *Symmetries in Science VII: Dynamic Symmetries and Spectrum-Generating Algebras in Physics*, edited by B. Gruber and T. Osaka (Plenum, New York, 1993).

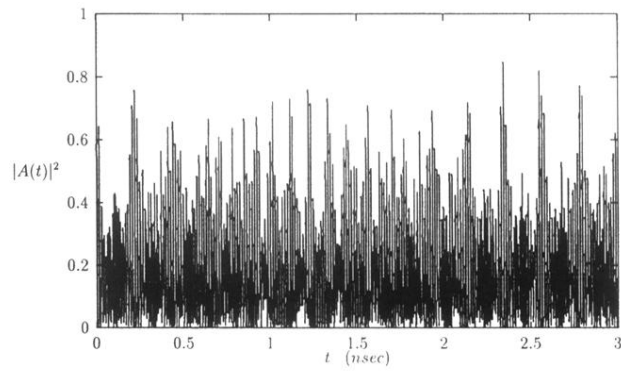


FIG. 1. Absolute square of the autocorrelation function for rubidium radial squeezed states with $N^* \simeq 45.35$ as a function of time in nanoseconds.