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# Synchronization of Raman Transitions in Highly Excited Hydrogen Atoms: A New Proposal for Measuring the Rydberg Constant

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**Abstract.** We present an analysis of the Raman interaction between a Rydberg atom and ultrashort light pulses. An application of the synchronization of quantum transitions to a simple atomic system (the hydrogen atom) is demonstrated. This is a direct way of measuring times and frequencies of microwave transitions between the high-lying atomic states using ultrashort light pulses. The results and analysis represent a new method for measuring the Rydberg constant.

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The synchronization of quantum transitions by ultrashort pulses is a new method for directly measuring the periods or frequencies of natural oscillations in atoms and molecules [1, 2]. The main features of the method are as follows: (i) The synchronization of quantum transitions is based on the interaction of atomic systems with perturbation pulses of a duration shorter than a period of the atomic oscillations under investigation. (ii) The phenomenon is not critically dependent on the nature of the pulse's perturbation. The latter may be an electric or magnetic field, a light, a collision with another particle, etc. (iii) If they interact with a pair of perturbation pulses delayed in time, atoms or molecules make quantum transitions which are synchronous with natural oscillations. The first of the pulses excites atomic oscillations and the second constrains the atoms to make synchronous transitions. (iv) In the time between the short pulses the atomic system is not perturbed by any measurement fields and thus measurement does not influence the atomic frequencies. (v) The interaction between an atom and a pair of time-separated light pulses depends on the time delay $T$ but not on the difference of their optical phases.

Here we demonstrate an application of the method to the simplest atomic system the hydrogen atom. The main spectroscopic aspect of investigations of the hydrogen atom is the measurement of atomic transition frequencies for determination of the fundamental Rydberg constant and a test of quantum electrodynamics.

We present a way of measuring times and frequencies of microwave transitions between the high-lying atomic states by using ultrashort light pulses. We start with a brief analysis of the physical processes taking place when the Rydberg atom interacts with a short pulse.

## 1. Interaction Between the Rydberg Atom and an Ultrashort Light Pulse

Let a hydrogen atom be excited into the Rydberg state $|n_0\rangle$ (Fig. 1), with $n_0$ being the principal quantum number ($n_0 \gg 1$). The frequency intervals between $|n_0\rangle$ and nearby states $|n_0 \pm 1\rangle$ are approximately equal to the frequency $\omega_0 = n_0^{-3} = 2\pi/T_0$, where $T_0$ is the orbital period, and atomic units ($e = \hbar = m = 1$) are used. We assume that the angular momentum $l_0$ of an electron in the atomic state $|n_0\rangle$ is much less than the principal quantum number $n_0$. This corresponds to small changes of momentum $\Delta l \ll n_0$ in a laser excitation of the Rydberg state $|n_0\rangle$ from the atomic ground state.

We consider an interaction between the Rydberg atom and the light pulse

$$E(t) = Eg(t)\exp(-i\omega t) + \text{c.c.},$$

where $E$, $\omega$ and $g(t)$ are the amplitude, the carrier frequency and the pulse shape of the optical field, respectively. The duration of the light pulse

$$\tau = \int_{-\infty}^{\infty} dt\, |g(t)|^2$$

is assumed to be shorter than the inverse orbital frequency but longer than the inverse ionization energy ($1 \geq \omega_0\tau \gg n_0^{-1}$).

This interaction between the Rydberg atom and the light pulse may be followed by (i) the one-photon ionization; (ii) the transition into a low-lying bound state with the emission of a photon; (iii) the two-photon Raman

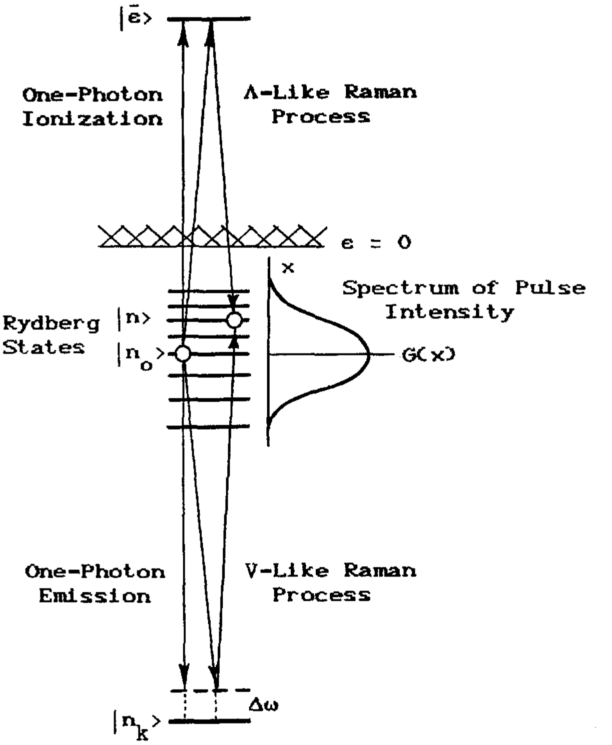

**Fig. 1.** Interaction between the Rydberg atom and an ultrashort light pulse

transitions $|n_0\rangle \to |n\rangle$ via the continuum; (iv) the two-photon Raman transitions $|n_0\rangle \to |n\rangle$ via bound states.

The probability of the one-photon ionization for the duration $\tau$ may be found using Fermi's "golden" rule

$$W_i = 2\pi |d_{n_0\bar{\varepsilon}} E/\hbar|^2 \tau\,, \tag{1}$$

where $d_{ik}$ is a projection of the dipole moment onto the field direction for the transition $|i\rangle \to |k\rangle$, $\bar{\varepsilon} = \omega - 1/(2n_0^2)$ is the energy (in a.u.) of a free electron.

The probability of the stimulated one-photon transition $|n_0\rangle \to |\bar{n}\rangle$ into a low-lying bound state is given by

$$W_e = |d_{n_0\bar{n}} E/\hbar|^2 \left| \int_{-\infty}^{\infty} dt g(t) \exp(\mathrm{i}\Delta\omega t) \right|^2 , \tag{2}$$

where $\Delta\omega = \omega_{n_0\bar{n}} - \omega$. This probability is negligible for the detuning $|\Delta\omega| \gg \tau^{-1}$.

As the spectrum of a light pulse is broader than the interlevel distance $\omega_0$, a two-photon Raman excitation of the superposition of Rydberg states is possible. After the light pulse, the state of the atom may be written in the form

$$|\Psi\rangle = \sum_n a_n |n\rangle\,,$$

where $a_n$ is the expansion coefficient and $|n - n_0| \ll n_0$. The total probability of detecting the atom in any of the bound states $|n\rangle$, which differ from $|n_0\rangle$, is equal to the sum of the individual probabilities of the transitions $|n_0\rangle \to |n\rangle$

$$W = \sum_{n \neq n_0} |a_n|^2 .$$

We find the probability $W$ using perturbation theory.

If the optical frequency $\omega$ is resonant with the transition $|n_0\rangle \to |\bar{n}\rangle$ into a low-lying state (i.e. $|\Delta\omega| \leq \tau^{-1}$), then the probability of the Raman excitation of the Rydberg manifold is given by

$$W = |E/\hbar|^4 \sum_{n \neq n_0} |d_{n\bar{n}} d_{\bar{n}n_0} G(\omega_{nn_0}, \Delta\omega)|^2 , \tag{3}$$

where

$$G(x, y) = \int_{-\infty}^{\infty} dt g(t) \exp[\mathrm{i}(x + y)t] \int_{-\infty}^{t} dt' g^*(t') \exp(-\mathrm{i}yt') .$$

The probability of the two-photon process may exceed the probability of stimulated one-photon emission if the number of Rydberg levels involved in the Raman process is large ($|n - n_0|_{\max} \gg 1$, i.e. $\omega_0\tau \ll 1$). To estimate the necessary light intensity, we use radial integrals $R_n^{n'}$ in the form (a.u.) [3]

$$R_n^{n'} = \xi (nn')^{11/6} (n^2 - n'^2)^{-5/3} , \tag{4}$$

where $\xi = 1.304$, $n - n' \gg 1$. Omitting the angular parts of the dipole matrix elements, we find from (2–4) that the inequality $W/W_e \geq 1$ is valid for the laser pulse energy (a.u.)

$$I\tau \geq (2\pi\xi)^{-2} c \bar{n}^{-11/3} ,$$

where $c = 137$, $I$ is the intensity, and we have used two approximations (for $1 \ll (\omega_0\tau)^{-1} \ll n_0$): $d_{n\bar{n}} d_{\bar{n}n_0} \approx |d_{\bar{n}n_0}|^2$ and

$$\sum_n |G(\omega_{nn_0}, \Delta\omega)|^2$$
$$\approx T_0 \int_{-\infty}^{\infty} dt |g(t)|^2 \left| \int_{-\infty}^{t} dt' g(t') \exp(\mathrm{i}\Delta\omega t') \right|^2 \approx T_0 \tau^3 .$$

For $\tau \cong 10^4$ ($\tau \leq \omega_0^{-1} = n_0^3$) and $\bar{n} \leq 10$, the intensity should be $I \geq 10^{-7}$.

In the nonresonant case ($|\Delta\omega| \gg \tau^{-1}$), we cannot neglect the contribution of continuum states $|\varepsilon\rangle$ to the Raman process $|n_0\rangle \to |\Psi\rangle$ when the detuning $\Delta\omega$ is too large. The probability $W$ is

$$W = W_\Lambda + W_V ,$$

where $W_\Lambda$ and $W_V$ are the probabilities of $\Lambda$- and $V$-like Raman processes, respectively (the corresponding expansion coefficients $a_{n\Lambda}$ and $a_{nV}$ of the state $|\Psi\rangle$ are mutually orthogonal in the complex plane). We find

$$W_\Lambda = \pi^2 |E/\hbar|^4 \sum_{n \neq n_0} |d_{n\bar{\varepsilon}} d_{\bar{\varepsilon}n_0} G(\omega_{nn_0})|^2 , \tag{5}$$

where

$$G(x) = \int_{-\infty}^{\infty} dt |g(t)|^2 \exp(\mathrm{i}xt)$$

is the spectral density of the field intensity, and

$$W_V = |E|^4 \sum_{n \neq n_0} |D_{nn_0} G(\omega_{nn_0})|^2 , \tag{6}$$

where $D_{nn_0} = \sum_{n_k}(d_{nn_k} d_{n_k n_0} \hbar^{-2} \Delta\omega_k^{-1})$ is the two-photon matrix element, and $\Delta\omega_k = \omega_{n_0 n_k} - \omega$.

The ratio of the contributions of $\Lambda$- and $V$-like Raman processes is (a.u.)

$$W_\Lambda / W_V \cong \Delta\omega_{\mathrm{eff}}^2 \omega^{-3},$$

where $\tau^{-1} \leq \Delta\omega_{\mathrm{eff}} \leq \omega \leq 1/2$, $\Delta\omega_{\mathrm{eff}} = \omega_{n_0 n_{\mathrm{eff}}} - \omega$, with the effective number $n_{\mathrm{eff}}$ corresponding to the estimation of a radial part of a two-photon matrix element by the formula $D_{nn'} \approx D_{nn} = (e/\hbar)^2 |R_n^{n_{\mathrm{eff}}}|^2 \times (\Delta\omega_{\mathrm{eff}})^{-1}$, and we have used the substitutions (a.u.) $R_{n'}^{E_n} = n^{3/2} R_{n'}^n$ (the renormalization of wavefunctions) and $n \to i/p$ ($p$ is the radial momentum of a free electron) to calculate the probability (5).

The one-photon ionization may be suppressed by the two-photon Raman process at a light intensity (a.u.)

$$I \geq \pi^{-1} \xi^{-2} c (2\omega)^{1/3} \Delta\omega_{\mathrm{eff}}^2, \tag{7}$$

where we have used (1, 4, 6) and the approximation [for $1 \ll (\omega_0 \tau)^{-1} \ll n_0$]

$$\sum_n |G(\omega_{nn_0})|^2 \approx T_0 \int_{-\infty}^{\infty} dt |g(t)|^4 \approx T_0 \tau .$$

In the case $(\omega_0 \tau)^{-1} \cong 1$ the right-hand part of (7) should be multiplied by $T_0/\tau$.

## 2. Interaction Between the Rydberg Atom and a Pair of Light Pulses

The time evolution of the superposition of Rydberg states generated by one light pulse manifests quantum beats of states with different quantum numbers $n$ [4, 5]. The delayed light pulse which follows after a time $T$ generates a new coherent superposition of Rydberg states, and this gives the interference with the high-lying superposition of states excited by the first light pulse.

The probability of detecting an atom in the Rydberg manifold after the second light pulse is equal to the sum of the individual probabilities of Raman transitions $|n_0\rangle \to |n\rangle$. For a pair of time-separated light pulses, the pulse shape $g(t)$ is replaced by $g(t) + g(t-T)$. Taking into account radiative decay we find [compare with (5, 6)]

$$W(T) = \sum_{n \neq n_0} W_n(T), \tag{8}$$

where the individual probability is given by

$$\begin{aligned} W_n(T) = {} & |E|^4 \exp(-\gamma_{n_0} t_{\mathrm{ex}}) \{ (|D_{nn_0}|^2 + \pi^2 \hbar^{-4} |d_{n\bar{\varepsilon}} d_{\bar{\varepsilon} n_0}|^2) \\ & \times |G(\omega_{nn_0})|^2 \exp[-\gamma_n (t - T)] \\ & \times [\exp(-\gamma_{n_0} T) + \exp(-\gamma_n T) \\ & + 2 \exp(-\gamma_{n_0} T/2 - \gamma_n T/2) \cos(\omega_{nn_0} T)] \}, \end{aligned} \tag{9}$$

where $t_{\mathrm{ex}}$ is the time interval between excitation of the initial Rydberg state $|n_0\rangle$ and the first ultrashort light pulse, $\gamma_k$ is the decay rate of the state $|k\rangle$, $t$ is the elapsed time ($t - T \gg \tau$).

## 3. Detection of the Rydberg-State Superposition

We assume that after the interaction between an atom and the two light pulses, Rydberg states of the atom will be detected by the selective Stark ionization [6] to independently find the results of the excitation of each Rydberg state $|n\rangle$ (Fig. 2). If the ionizing electric field is increased, the current observed in an ion detector will be a sequence of pulses. Each of the pulses corresponds to the selective ionization of one of the Rydberg states from $|n_{\max}\rangle$ to $|n_{\min}\rangle$. The total electric charge received by the detector in the time interval $t_{\max} - t_{\min}$ (ignoring the central pulse) is proportional to the probability of the excitation of the Rydberg manifold.

If the second light pulse arrives in phase with the beating between one of the states $|n\rangle$ and the initial state $|n_0\rangle$ ($\omega_{nn_0} T = 2\pi k$), then a maximum of the respective ionization signal may be detected, but in the case of antiphase arrival ($\omega_{nn_0} T = \pi(2k - 1)$), the ionization signal will be absent, see (9). This individual probability behaviour coincides exactly with that occured in the synchronization

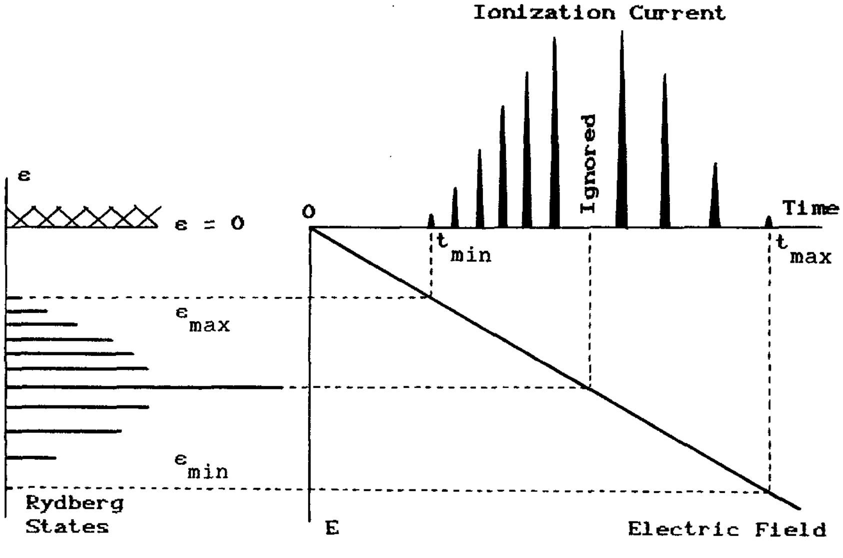

Fig. 2. Detection of Rydberg states by selective Stark ionization

of quantum transitions for two-level atomic systems [2]. Observation of the behaviour as a function of the delay time $T$ allows direct measurements of the times of quantum transitions.

## 4. Computer Experiments

Results of computer calculations for the total probability (8,9) of the excitation of the Rydberg-state superposition by pairs of light pulses at different delay times $T$ are shown in Fig. 3. The case refers to short light pulses exciting a Rydberg manifold of approximately 20 states. The Fourier transform of this signal permits us to determine the frequencies of quantum transitions. The Fourier transformation was performed for the calculated signal, with an observation time equal to 600 periods $T_0$ of quasiclassical electron motion. The two lines in Fig. 4 refer to the quantum transitions between the initial state $|n_0\rangle$ and adjacent states $|n_0 \pm 1\rangle$. The linewidth at half-maximum is the inverse time of the observation. The accuracy of the determination of resonance frequencies depends on the observation time and on the increment of the delay time. We find two resonance frequencies with an accuracy of order $10^5$.

## 5. Discussion

The upper limit of the observation time $T$ is the lifetime of the Rydberg state. For a Rydberg state with a small angular momentum $l \ll n$ the radiative lifetime in units of the period $T_0$ is [3] $T_{nl}/T_0 = (\sqrt{3}/8)c^3 l^2$. Thus, the accuracy in measuring resonance frequencies can be of the order of $10^9$–$10^{10}$ ($l = 1$–$10$). For more accurate measurements, atoms in high angular momentum states ($l \cong n$) should be used. But such atomic states ($n_0 \gg 1$, $l_0 \cong n_0$) are not dipole-coupled with low states ($\bar{n} = 1$–$10$), so in this case the Raman process of excitation of nearby Rydberg states will involve strongly nonresonant dipole transitions between the states. For example, if an atom is initially in the circular state $|n_0, l_0 = n_0 - 1\rangle$, the adjacent state s with $n = n_0 + 1$ may be excited by the Raman process

$$|n_0, l_0 = n_0 - 1\rangle \to |\bar{n} = n_0 - 1, \bar{l} = l_0 - 1\rangle \to |n_0 + 1, l_0\rangle .$$

The product of the corresponding radial integrals is [3a] (a.u.)

$$R^{n,n-1}_{n-1,n-2} R^{n+1,n-1}_{n-1,n-2} = 3n^{-1} .$$

Thus the individual probability is $W_{n+1} \propto n^{-2}$, i.e. an increase in the accuracy of frequency measurements by a factor $n^2$ for circular atoms, requires light pulses whose intensity is increased by $n^2$ compared to that for the excitation of small angular momentum states.

We have thus identified new possibilities for frequency measurements by using short light pulses rather than a microwave field. The latter method includes only one dipole transition between two adjacent states and, due to the cw interaction, the transition is broadened by the microwave field. In our case a light pulse excites several

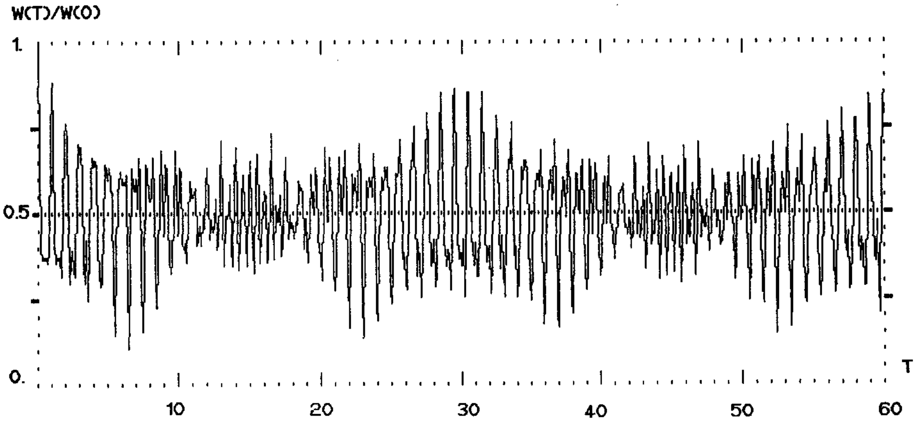

**Fig. 3.** Probability of the excitation of the Rydberg-state superposition by pairs of light pulses vs. the interpulse time $T$, with $T$ measured in units of the orbital period $T_0$ ($n_0 = 90$, $\tau\omega_0 = 0.5$)

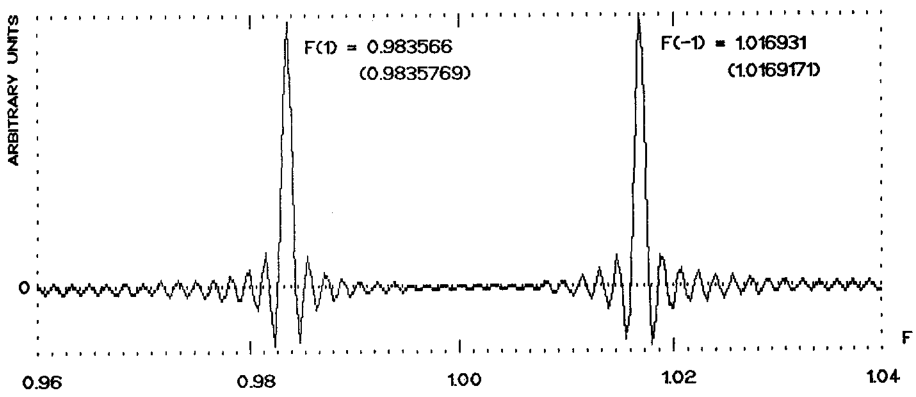

**Fig. 4.** Portion of the Fourier spectrum. The values in brackets are theoretical ones. $F$ is frequency in units of $\omega_0$, $F(\Delta n) = \omega_{nn_0}/\omega_0$, $\Delta n = n - n_0$

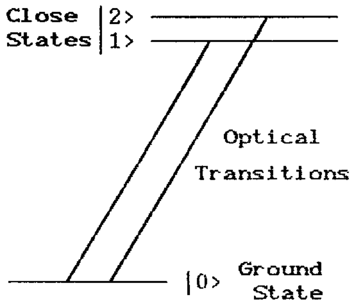

**Fig. 5.** Typical scheme of an interaction between an atom and a short light pulse. If the transition $|0\rangle \rightarrow |1, 2\rangle$ is a forbidden one, then a two- or multi-photon process is assumed for its excitation

forbidden transitions, and the method is free from power broadening.

At first sight, the method considered here seems very similar to methods such as time-Fourier Raman spectroscopy [7], the photon echo in the Rydberg atom [8], the time-delayed Raman detection of Rydberg wave packets [5] and some others. To understand the major differences between our method and other known laser spectroscopic methods, we give a brief analysis of the excitation of two nearby atomis states $|1\rangle$ and $|2\rangle$ from the ground state $|0\rangle$ by a short light pulse (Fig. 5). The total number of final excited states may be more than two. Such a scheme is typical for the methods mentioned above [7, 8, 5] and differs from the scheme of Fig. 1 due to the excitation of atomic oscillations at optical frequencies $\omega_{10}$, $\omega_{20}$ which are much higher than $\tau^{-1}$, $\omega_{21}$. Thus the interaction between the atom and the second light pulse will be effective if this second pulse is coherent with the high-frequency atomic oscillations and has an optical phase coinciding with the phase of the first light pulse. The following quantitative consideration confirms this.

For $\tau \leq \omega_{21}^{-1}$, after the interaction with a single light pulse, the excited atomic state will be the superposition

$$|\Psi\rangle = a_1|1\rangle + a_2|2\rangle ,$$

where $a_k = \mathrm{i}(Ed_{k0}/\hbar)\tilde{G}(\omega_{k0} - \omega)$, $k = 1, 2$; $\tilde{G}(x)$ is the spectral density of the optical field, and $a_0 \approx 1$. The interaction with the second pulse delayed by time $T$ gives

$$|\Psi_T\rangle = \sum_{k=1,2} a_k[1 + \exp(\mathrm{i}\varphi + \mathrm{i}\Delta_k T)]\,|k\rangle ,$$

where $\varphi$ is the phase difference between the two light pulses, $\Delta_k = \omega - \omega_{k0}$, and we assume that the pulse intensities are equal. The individual probability of detecting the atom in the excited state $|k\rangle$ is of the form

$$W_k(T) = |\langle k\,|\,\Psi_T\rangle|^2 = |a_k|^2[1 + \cos(\varphi + \Delta_k T)] . \qquad (10)$$

We see that the individual probability contains the phase $\varphi + (\omega - \omega_{k0})T$, in contrast to the pure atomic phase $\omega_{nn_0}T$ appearing in our method; see (9) and also [2]. The result (10) is the same as in the method of time- or space-separated fields. The second light pulse in this case probes the high-frequency dipole moment $d_{k0}(t)$, and thus it is the difference of the atomic phase $\omega_{k0}T$ and the optical phase of $\omega T + \varphi$ that appear in (10). This makes direct measurements of time impossible.

The pure atomic phase $\omega_{21}T$ appears only in the total probability $W = W_1 + W_2$ of detecting the atom in any excited state, but a term with this phase is multiplied by a term with the laser phase:

$$\Delta W(T) \propto \cos(\omega_{21}T/2)\cos[\varphi + (\Delta_1 + \Delta_2)T/2] . \qquad (11)$$

This result corresponds to probing at time $T$ the usual quantum beats between two dipole moments $d_{10}(t)$ and $d_{20}(t)$. These beats *in real time* may be detected by observing the fluorescence from the states $|1\rangle$ and $|2\rangle$ [9] or by stimulated light scattering [5, 7]. From (11) we see that in order to observe atomic oscillations at the frequency $\omega_{21}$ the light pulses should be mutually coherent and also coherent with the optical oscillations at $\omega_{10}$ or $\omega_{20}$.

On the other hand, the method of synchronization of quantum transitions is based on oscillations at natural frequencies in *individual population probabilities* of states. These oscillations do not occur in real time, the probabilities depend on the pure atomic phases $\omega_{nn_0}T$ *parametrically*, and one may detect this dependence at any time after the perturbation of an atom by a pair of pulses during the atomic lifetime. The total probability (8) consists of the individual probabilities (9), and each of these is independent of the optical phases.

## 6. Conclusion

The results and analysis given here represent a new method for measuring the Rydberg constant. The method may also be used for frequency and time measurements in molecules.

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