Suppression of angular-momentum mixing in precision solutions of the Schrödinger equation for photoexcitation of Rydberg states

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(Received 5 April 2001; published 24 April 2002)

Numerical integration of the Schrödinger equation for the resonant single-photon excitation from the $1s$ to $10p$ state in atomic hydrogen has been used to produce solutions converged to a precision of a few parts per million. At all intensities investigated (in the range 10–100 TW/cm^2), the population in the states having angular momentum higher than $\ell=1$ after a narrowband (500 fs) laser pulse are found to be neglible. This shows that off-resonant states can effectively suppress Raman-like transitions to degenerate states of higher angular momentum. Instead of such mixing, strong Rabi-like oscillations between $1s$ and the np Rydberg series are observed.

DOI: 10.1103/PhysRevA.65.055402 PACS number(s): 32.80.Rm

It has been recently suggested that the very large dipole coupling between degenerate Rydberg states could cause effective population transfer between such states at comparatively low intensity [1]. This mixing of angular momenta would manifest itself among other things in the generation of high harmonics. More extensive considerations, taking into account the existence of the many neighboring Rydberg manifolds, have shown that such levels might conspire to counteract this mixing [2]. Despite the fact that coupling with such levels is much weaker than those within the resonant manifold, a large number of such states that are available makes them nevertheless important. This mixing suppression mechanism has been called multistate off-resonant quantum coherence (MORQ).

MORQ has been criticized [3,4] because it was first demonstrated in a model system with properties that approached that of a true atom only in the limit of infinitely high principal quantum number n (such as constant level spacing). This casted some doubt on how well the mechanism would perform under less idealized conditions. Especially at lower n, the Rydberg level spacing varies appreciably over the large range of off-resonant states needed to effect the suppression.

In this paper we, therefore, investigate a more realistic description of a hydrogen atom, driven by a laser that resonantly excites the (initial) $1s$ ground state to the $n=10$ Rydberg level (laser frequency $\omega=0.495$). The laser field is described in the dipole approximation. Since the wavelength of the light is 1739 bohrs, much larger than the size of the involved atomic states, this should be reasonable. Furthermore, it allows comparison with earlier work, which was using the dipole approximation as well.

For the more realistic system no analytical solutions to the Schrödinger equation can be obtained. However, numerical methods for integrating partial differential equations combined with progress in computer technology have reached a point where solutions can be obtained to almost any desired precision [5–7]. In linear polarization, cylindrical symmetry reduces the problem to a two-dimensional one. Unlike most two-dimensional problems, the current one is not entirely trivial: the small level spacing of the Rydberg states (which reflects their long orbit times) requires laser pulses of narrow bandwidth to excite them selectively, and such pulses contain extraordinarily large numbers of cycles. In addition, Rydberg states cover a lot of space, necessitating a large grid.

In the present paper, we consider a laser pulse of 3150 cycles, with a sine-square envelope. This pulse most closely resembles the Gaussian pulses used by other authors [8], with a full width at half maximum duration of about 500 fs. Representation on an angular-momentum, radial-position grid with constant radial step has been shown to allow efficient integration of the Schrödinger equation for this kind of problem [9]. The advantage of grid methods is the local nature of the coupling: A finite-difference representation of the radial derivatives couples only neighboring radial points, while the angular-momentum selection rule $\Delta\ell=\pm1$ (in the dipole approximation) guarantees the same in the ℓ dimension. This not only makes the propagation very efficient, but also allows for a good *a priori* check on convergence with grid size: if the wave packet never reaches the boundary of the integration box at any time during the calculation, it could not possibly have gone beyond the grid edges. Note that representation of the wave function on a basis of atomic (bound and continuum) eigenstates is much less transparent, since such states couple to all other states of allowed angular momentum, also to those not taken into account. This essentially brings the entire wave function in contact with the ''box boundary'' all the time.

The outer turning point of the $n=10$ Rydberg manifold is located at $2n^2=200$ bohrs from the nucleus, and to make sure that weakly bound electrons would not be disturbed by the grid boundary we took the latter at 500 bohrs. Electrons ionized by two-photon absorption in principle would travel up to 40 000 bohrs during the pulse, and it would be needlessly expensive to try to prevent them from reaching the boundary. Instead, an absorbing potential prevents reflections of this ionization current, in order to minimize the effects of the finite grid size on the wave function in the neighborhood of the atom. The part of the continuum that could be responsible for Raman-like two-photon transitions [10] between Rydberg states of different ℓ, is thus fully and accurately represented.

For weakly bound or free electrons the velocity gauge is usually the most efficient one for computation [11], since the

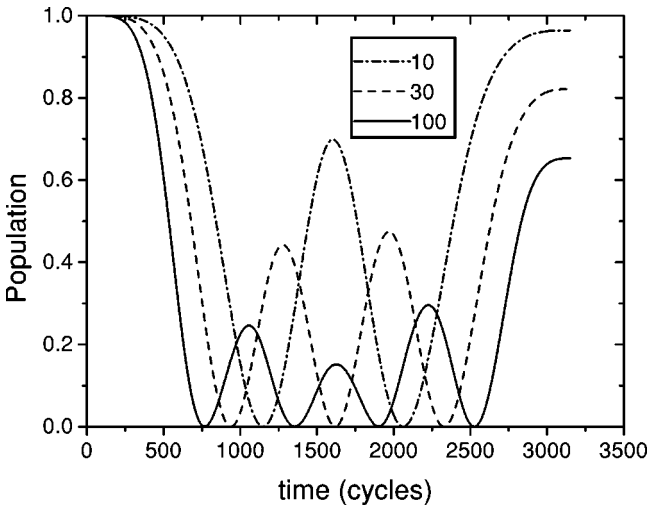

FIG. 1. Total *s*-state population in a hydrogen atom exposed to a sine-square laser pulse as a function of time. The curves are sampled at electric-field maxima (where angular momentum means the same in length and velocity gauge). The driving pulse is tuned to the 1*s*-10*p* transition. The intensities are 10, 30, and 100 TW/cm^2.

huge value of the $\mathbf{E}\cdot\mathbf{r}$ potential at large r makes the behavior of the wave function in the length gauge rather wild, while $\mathbf{A}\cdot\mathbf{p}$ is usually quite small. The wave functions in the two gauges are related by a simple multiplicative phase factor $\exp(iAr\cos\vartheta)$. In the current problem, due to the high laser frequency, the vector potential $A=E_0/\omega$ is not yet too high, and at $E_0=0.0293$ the complex phase of the gauge-transform factor does not exceed $30\cos\vartheta$ anywhere in the box (and is limited to only $12\cos\vartheta$ in the classically allowed region of an $n=10$ state). The angular dependence introduced by this can be represented by about 20 extra angular momenta, so that length-gauge calculations are not entirely impossible. Thus both length- and velocity-gauge calculations were performed, the comparison providing an independent convergence check.

Integrations were performed for pulses of three different peak intensities, 10, 30, and 100 TW/cm^2 (corresponding to peak fields of 0.016 88, 0.0293, and 0.053 38 a.u., respectively). In all cases, the ground state was completely depleted on the rising edge of the pulse, by excitation to high Rydberg states (Fig. 1). Ionization by a two-photon process apparently hardly occurs: it would take electrons resulting from this process only about 40 cycles to reach the grid end where their absorption causes a decrease of the wave-function norm, and such a decrease is hardly observed (less than 1% over the entire pulse). Instead, the entire population goes into high Rydberg orbits. After the ground-state population hits zero [12], population is pumped back from these Rydberg states to the ground state in a Rabi-like oscillation cycle. Unlike Rabi oscillations in a two-level system, however, the population never goes back entirely to the ground state, although it can go entirely to the Rydberg states several times during the pulse.

Due to the narrow bandwidth of the light, the calculation is extremely sensitive to the frequencies of the involved energy levels. In the Crank-Nicholson approximation $(1+iH\tau)^{-1}(1-iH\tau)$, used to implement the atomic propagator, the frequency with which an eigenstate evolves is not equal to the eigenvalue E of the Hamiltonian H, but rather to $1/\tau\arctan E\tau$. As a consequence, the effective level energies become a function of the temporal step size 2τ. Rapid convergence with respect to spatial and temporal step sizes is only obtained if we keep the ground-state frequency fixed to its asymptotic value of -0.5, by tweaking the atomic potential in the first grid point [13]. An energy shift of 10^{-4} hartree already results in a markedly different behavior of the solution, where the ground-state population no longer dips all the way to zero, but stays well above 5%.

The grid spacing was chosen as 0.25 bohr. The fourth-order finite-difference scheme used [9] is extremely accurate for this step size on the low momenta of Rydberg states, and only electrons that are close to the nucleus have momenta high enough that effects of the discretization are noticeable. The ground state suffers most from this, and without any tweaking it would have energy of $-0.500\,37$. The integration in the velocity gauge needs only five angular momenta ($\ell=4$ has a maximum population of 1.6×10^{-9}), and with 100 steps per optical cycle it is converged at the level of a few parts per million provided we correct the potential in the first point such that the corresponding eigenvalue of the Hamiltonian becomes $-0.500\,168$ (so that its effective frequency is $-0.500\,000$).

The length-gauge calculation (only attempted at $E_0=0.0293$) is more difficult to converge; it needs about 20 angular momenta, and even at 400 steps per cycle the results deviate from the converged limit by about 0.1%. (Clear quadratic convergence with respect to τ, however, makes extrapolation to this limit easy, and the extrapolated values coincide with the velocity-gauge results.) The more demanding behavior with respect to the time step can be explained by the high instantaneous value of the $\mathbf{E}\cdot\mathbf{r}$ part of the Hamiltonian at large distance: at the outer turning point this energy can go up to 6 hartree, causing a very rapid phase evolution that needs a very small time step for accurate description.

Analysis of the wave function in terms of angular momenta shows that only the *p* states contain significant population in the velocity gauge. Of the higher angular momenta, only the *d* space has a population of a few parts per 10^4, mostly consisting of the continuum electrons from two-photon ionization in transit to the grid end. The other populations stay below 10^{-7} at any time. In the length-gauge calculation, the same is true only at times of electric-field maxima. At those times length and velocity gauges coincide, so any differences here can only be due to calculational error. At other times, the length-gauge population is spread out over a broad range of angular-momentum states. At electric-field zero crossings near the peak of the pulse the distribution over angular momenta is approximately flat up to $\ell=10$, and tails off quickly beyond that until it reaches the 10^{-5} level at $\ell=19$.

The laser pulse is designed such that it has zero dc component, so that after it is finished the two gauges also coincide. At all intensities the calculations predict similar results

for the final situation, distributing the population between s and p states. Practically all continuum electrons have escaped the box by that time, and the population in the higher angular momenta is less than 10^{-7}. Energy analysis in the various subspaces shows that the s population resides entirely in $1s$ (less than 10^{-14} in $10s$), while the p population is almost entirely in $10p$.

In conclusion, we can say that the MORQ mechanism seems to suppress angular-momentum mixing just as perfectly in the case of Rydberg states as low as $n=10$ in a real hydrogen atom, as it did in the rather idealized and simplified model for such states in the limit $n\rightarrow\infty$ [2]. This is true despite the high depletion of the ground state, which might seem surprising in view of the fact that in the original MORQ demonstration ground-state depletion was completely neglected. The main effect causing the angular-momentum mixing suppression, however, was the dynamics within the Rydberg manifold, which was treated in a completely nonperturbative way. How strongly the ground state is then coupled to this manifold is of no consequence.

The conclusion that MORQ works in a realistic atom also contradicts an earlier calculation [8], which found results similar to ours for short (6 fs) pulses, but strong mixing in long-pulse conditions nearly identical to those used here. This latter calculation was done on a basis set of 897 atomic eigenstates in the length gauge. To compare the two calculations, we can express the operators used in the grid calculation on the basis of eigenfunctions of the discretized atomic Hamiltonian. The matrix representation of the two operators relevant for the time evolution (the atomic Hamiltonian and the laser interaction) in this basis set coincides with an extremely high precision to the exact representation, at least in the subspace of the grid calculation spanned by the discretized eigenvectors corresponding to states used in Ref. [8].

The accuracy with which the grid representation of the problem approaches the true (continuous) one for the same number of angular momenta and the same box size is essentially determined by how well the radial overlap integrals are approximated by a sum over grid points. The main error for the type of functions occurring in this problem comes from near the origin, and thus affects the low angular momenta most. The energies of s and p states are found to be accurate to a few microhartrees, and the dipole matrix elements for s-p transitions have errors less than 0.1% of their value. The Hilbert space spanned by the grid calculation thus seems to completely include that spanned by the 897 states of the eigenfunction basis, and should accurately copy all the behaviors within that space. The only explanation for the qualitatively very different results that we could think of is, therefore, that an important part of the dynamics goes on outside this space (i.e., the eigenstate calculation of Ref. [8] was not yet fully converged).

This work was a part of the research program of FOM (Fundamental Research on Matter), which was subsidized by NWO (Netherlands Organization for the Advancement of Scientific Research). I thank Jan Petter Hansen for useful discussions.

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