Numerical integration of the time-dependent Schrödinger equation for an atom in a radiation field

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We describe an approach for numerically integrating the time-dependent Schrödinger equation for an atom in a radiation field. The time propagation is based on the split-operator technique, with the full Hamiltonian split into two parts, the atomic Hamiltonian and the atom-field interaction. Both parts are represented on a complex Sturmian basis. The method is relatively efficient; ionization yields and level populations for atomic hydrogen can easily be computed on a workstation for modest pulse durations (e.g., 50 cycles or so) and modest intensities (e.g., of order 10^{15} W/cm^2 for a frequency of 0.2 a.u.). We present results of an application of the method to atomic hydrogen, and to illustrate the performance we compare our results with those obtained previously by Kulander [Phys. Rev. A **35**, 445 (1987)]. We also illustrate the stabilization of atomic hydrogen against ionization by an intense high-frequency field, and the sensitivity of the ionization yield to the relative phase in the case where the field is bichromatic with one field a harmonic of the other.

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I. INTRODUCTION

During the past few years, numerous approaches have been suggested for solving the time-dependent Schrödinger equation for an atom in a radiation field [1]. Despite impressive advances, for example, the calculation of high-order peaks in the photoelectron energy spectrum [2], storage and execution time requirements still pose significant obstacles to extensive computation. In this paper we suggest a method that holds some promise for improving computational efficiency. We have tested the method by carrying out calculations of rates and yields for multiphoton ionization of atomic hydrogen, and we present some results that illustrate several interesting features. In particular, we demonstrate the stabilization of atomic hydrogen against ionization by an intense high-frequency field [3], and, in the case where the field is bichromatic with one field a harmonic of the other, we illustrate the sensitivity of the ionization yield to the relative phase [4].

We describe the radiation by a classical field, within the dipole approximation. The full Hamiltonian is $H(t) \equiv H_a + V(t)$, where H_a is the Hamiltonian of the atom and $V(t)$ is the interaction of the atom with the radiation. We represent H_a and $V(t)$ on a basis consisting of products of complex radial Sturmian functions and spherical harmonics. The Sturmian functions [5] have many useful properties which allow matrix elements involving Coulomb and dipole interactions to be calculated recursively, and with little roundoff error, and they have been shown to give a good representation of atomic wave functions [6]. As in previous Floquet calculations [7], we choose the wave number of the Sturmian functions to be complex, so as to allow for the absorption of the flux due to ionization. It is well known that a real basis results in reflections of the emitted photoelectrons from the

boundaries of the basis, and in order to minimize these reflections a very large basis must be used. Thus the basis size can be substantially reduced by allowing for absorption of flux [8]. The time propagation of the state vector is based on the split operator technique [9], with $H(t)$ split into the two parts H_a and $V(t)$. This technique calls for H_a and $V(t)$ to be exponentiated, which at first sight might seem to be a drawback. However, if a matrix can be readily diagonalized, its exponentiation is trivial. Now, the matrix representation of H_a is block diagonal (in the orbital angular momentum quantum number) and can be diagonalized very rapidly. Furthermore, since H_a is time independent, it need be diagonalized only once. Although $V(t)$ is time dependent, this time dependence has a very special form: It is contained entirely in a c-number which may be factored out of $V(t)$. Thus $V(t)$ also need be diagonalized only once. Furthermore, the symmetries of $V(t)$ can be used to significantly expedite this diagonalization. Consequently, it is practical to exponentiate both H_a and $V(t)$ [10]. Finally, the symmetries of the problem may be used to significantly reduce the number of matrix elements that must be calculated and stored in the time propagation.

In Sec. II we describe our method in more detail. In Sec. III we present our results. To illustrate the performance of the method, we compare our estimates of ionization rates with those obtained earlier by Kulander [11], as well as to those obtained by Chu and Cooper [12] using the Floquet method.

II. METHOD

The formal solution of

$$i\hbar \frac{d}{dt}|\Psi(t)\rangle = H(t)|\Psi(t)\rangle , \qquad (1)$$

subject to known boundary conditions at time $t = t_0$,

is $|\Psi(t)\rangle = U(t,t_0)|\Psi(t_0)\rangle$, where $U(t,t_0)$ is the time-evolution operator, which satisfies the group property $U(t,t_0) = U(t,t')U(t',t_0)$ for any triad of times t, t', t_0. Thus, if we divide the interval $t_0 \le t \le t_N$ into N subintervals $t_{n-1} \le t \le t_n$, $n = 1, \ldots, N$, we can express $U(t_N, t_0)$ as the product of N evolution operators $U(t_n, t_{n-1})$. Provided that $\delta_n \equiv t_n - t_{n-1}$ is sufficiently small, we have [9]

$$
\begin{aligned}
U(t_n, t_{n-1}) &= \exp\left[-i\frac{\delta_n}{\hbar} H\left(\frac{t_n + t_{n-1}}{2}\right)\right] [1 + O(\delta_n^3)] \\
&= \exp\left[-i\frac{\delta_n}{2\hbar} V\left(\frac{t_n + t_{n-1}}{2}\right)\right] \exp\left(-i\frac{\delta_n}{\hbar} H_a\right) \\
&\quad \times \exp\left[-i\frac{\delta_n}{2\hbar} V\left(\frac{t_n + t_{n-1}}{2}\right)\right] [1 + O(\delta_n^3)] ,
\end{aligned}
\tag{2}
$$

where the second step follows from using $e^{(A+B)\delta} = e^{(1/2)A\delta} e^{B\delta} e^{(1/2)A\delta}[1 + O(\delta^3)]$. We now write $V(t) = f(t)V$, where V is time independent, and we represent V and H_a on an *orthonormal* basis by matrices $\underline{V}$ and $\underline{H}_a$. Furthermore, we put these matrices in diagonal form, that is, we write

$$
\underline{H}_a = \underline{X} \, \underline{D}_a \underline{X}^{-1} ,
\tag{3}
$$

$$
\underline{V} = \underline{Y} \, \underline{D}_{\mathrm{int}} \underline{Y}^{-1} ,
\tag{4}
$$

where $\underline{D}_a$ and $\underline{D}_{\mathrm{int}}$ are diagonal matrices. Hence, if $\underline{U}(t_n, t_{n-1})$ is the matrix representation of $U(t_n, t_{n-1})$, we have

$$
\begin{aligned}
\underline{U}(t_n, t_{n-1}) &= \underline{Y} \, \underline{U}_{\mathrm{int}}(t_n, t_{n-1}) \\
&\quad \times \underline{M}_n \underline{U}_{\mathrm{int}}(t_n, t_{n-1}) \underline{Y}^{-1}[1 + O(\delta_n^3)] ,
\end{aligned}
\tag{5a}
$$

$$
\underline{M}_n \equiv (\underline{Y}^{-1}\underline{X}) \exp\left(-i\frac{\delta_n}{\hbar}\underline{D}_a\right) (\underline{Y}^{-1}\underline{X})^{-1} ,
\tag{5b}
$$

$$
\underline{U}_{\mathrm{int}}(t_n, t_{n-1}) \equiv \exp\left[-i\frac{\delta_n}{2\hbar} f\left(\frac{t_n + t_{n-1}}{2}\right) \underline{D}_{\mathrm{int}}\right] .
\tag{5c}
$$

Note that the matrices $\underline{X}$ and $\underline{Y}$ appear only [13] in the combination $(\underline{Y}^{-1}\underline{X})$, and that the inverses of $\underline{X}$ and $\underline{Y}$ may be computed immediately—the inverse of $\underline{X}$ is its transpose, and the inverse of $\underline{Y}$ is its Hermitian adjoint (see below). If we choose the time step to be constant, so that δ_n, and therefore $\underline{M}_n$ are independent of n, we need evaluate $\underline{M}_n$ only once, and the time propagation of the state vector reduces to the single multiplication of $\underline{M}_n$ with a vector at each time step. If we choose a variable time step, and in general this is preferable, at least two matrix-vector multiplications are required per time step. However, by utilizing the block-diagonal structures of $\underline{X}$ and $\underline{X}^{-1}$, and the special properties of $\underline{Y}$ and $\underline{Y}^{-1}$ (see below), these matrix-vector multiplications can be carried out rapidly, and it turns out that the number of operations per time step is the same whether a fixed or variable time step is used. In fact, we use the same (the latter) scheme whether the time step is fixed or variable.

Using atomic units, and writing

$$
K_l = -\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} ,
\tag{6}
$$

the radial Sturmian functions are solutions of the differential equation

$$
\left(K_l + i\frac{n\kappa}{r} - \frac{1}{2}\kappa^2\right) S_{nl}^\kappa(r) = 0 ,
\tag{7}
$$

with the asymptotic boundary condition that $S_{nl}^\kappa(r)$ behaves as $r^n e^{i\kappa r}$ for large r. The Sturmian functions satisfy the orthonormality condition

$$
\int_0^\infty dr \, S_{nl}^\kappa(r)(1/r)S_{n'l}^\kappa(r) = -i(\kappa/n)\delta_{nn'} ,
\tag{8}
$$

where we have chosen the normalization

$$
\int_0^\infty dr \, [S_{nl}^\kappa(r)]^2 = 1 .
\tag{9}
$$

We can analytically continue Eqs. (8) and (9) to arbitrary complex κ. Defining $\theta \equiv \pi/2 - \arg(\kappa)$, we choose $0 < \theta < \pi/2$, so that the basis functions can represent both the closed channels and the *outgoing* wave open channels of the exact wave function. Note that the Sturmian functions are not orthogonal; rather, the overlap matrix $\underline{S}_l$, whose elements are $\int dr \, S_{nl}^\kappa(r)S_{n'l}^\kappa(r)$, is *tridiagonal*. If $\underline{K}_l$ denotes the matrix representation of the kinetic energy operator K_l on this *non*orthogonal basis, we have, from Eqs. (7)–(9),

$$
\underline{K}_l = \frac{1}{2}\kappa^2 \underline{S}_l - \kappa^2 \underline{I}_l ,
\tag{10}
$$

where $\underline{I}_l$ is the identity matrix. We construct an *orthonormal* basis from the eigenvectors of $\underline{S}_l$. The matrix representation of K_l on this orthonormal basis is $\underline{\tilde{R}}_l\underline{K}_l\underline{R}_l$, where the tilde denotes the transpose of a matrix, and where $\underline{\tilde{R}}_l\underline{S}_l\underline{R}_l = \underline{I}_l$ and $\underline{R}_l\underline{\tilde{R}}_l = \underline{S}_l^{-1}$. Assuming that $\underline{R}_l$ is a square matrix, so that $\underline{\tilde{R}}_l\underline{R}_l = \underline{S}_l^{-1}$, we see from Eq. (10) that the eigenvalues of $\underline{\tilde{R}}_l\underline{K}_l\underline{R}_l$, and hence of K_l, are $\epsilon_{li} \equiv (s_{li} - 2)/(2s_{li})\kappa^2$, $i = 1, 2, \ldots$, where the s_{li}, $i = 1, 2, \ldots$, are the eigenvalues of $\underline{S}_l$. Both $\underline{R}_l$ and $\underline{S}_l$ are real for all κ, and since $\underline{S}_l$ is also symmetric the s_{li} are real. In general, the ϵ_{li} are complex, but when $\theta = 0$ (that is, when κ is positive imaginary) $\underline{K}_l$ is Hermitian and positive definite, and in this case the ϵ_{li} are real and positive. It follows that $0 < s_{li} \le 2$ for all κ. We exclude from our basis those eigenvectors of $\underline{S}_l$ that have eigenvalues s_{li} that are very small, since such eigenvectors are nearly linearly dependent, and the kinetic energy eigenvalues are very large (and give rise to rapid temporal oscillations in the time propagation, necessitating a very small time step). We also exclude those eigenvectors that have eigenvalues s_{li} very close to 2, since the kinetic-energy eigenvalues are very small, and by excluding these eigenvectors we avoid wastefully representing those very high Rydberg states that play almost no role. As a result of this reduction of the basis, $\underline{R}_l$ is not a square matrix.

From Eq. (8) we see that the Coulomb potential $-Z/r$ is diagonal on the nonorthogonal basis, with elements $iZ\kappa/n$. It follows that the hydrogen atom Hamiltonian is represented on the *orthonormalized* basis by the block-

diagonal matrix

$$\underline{H}_a = \frac{1}{2}\kappa^2\underline{I} + \tilde{\underline{R}}(\underline{D}_C - \kappa^2\underline{I})\underline{R} \;, \tag{11}$$

where the diagonal blocks are labeled by l, where $\underline{I}$ and $\underline{R}$ consist of diagonal blocks $\underline{I}_l$ and $\underline{R}_l$, respectively, and where $\underline{D}_C$ is a diagonal matrix whose diagonal elements in each block are $iZ\kappa/n$. The block diagonal matrix $\underline{X}$, which diagonalizes $\underline{H}_a$, may be obtained rapidly. Note that $\underline{H}_a$ is a symmetric matrix, and therefore $\tilde{X}X = X\tilde{X} = \underline{I}$. Since κ lies in the upper right quadrant of the complex plane, those eigenvalues of $\underline{H}_a$ which correspond to continuum levels are complex, and have negative imaginary parts (the arguments are approximately equal to -2θ), while those eigenvalues which correspond to bound levels remain (approximately) real (they have only very small negative imaginary parts). Therefore $\underline{U}(t, t_0)$ is not unitary, and in fact decays as t increases. This is reasonable; our basis can only describe the atom over some finite volume $\mathcal{V}$ of space, and the probability for finding the electron inside $\mathcal{V}$ diminishes as the atom ionizes. By choosing basis functions that can describe the correct *complex* boundary conditions, we do not need to introduce *ad hoc* absorbing walls at the boundary of $\mathcal{V}$ to avoid reflections of the photoelectron. To obtain the ionization probability at the end of the pulse, we simply compute the population in the bound states and subtract this from unity. However, since $\underline{U}(t, t_0)$ is not unitary, we cannot calculate the photoelectron energy spectrum, or the angular distribution, by projection onto the continuum states; rather, we must calculate the flux which passes through the surface of a sphere that is centered at the atomic nucleus and has a radius of a few atomic radii [14].

In the velocity gauge, we have (for a one-electron system) $V(t) = (1/c)\mathbf{A}(t) \cdot \mathbf{p}$, where $\mathbf{A}(t)$ is the vector potential, and where $\mathbf{p}$ is the canonical momentum (in the center of mass frame) of the electron, while in the length gauge we have $V(t) = \mathbf{F}(t) \cdot \mathbf{x}$, where $\mathbf{F}(t)$ is the electric field vector and where $\mathbf{x}$ is the position coordinate. As in the Floquet method [7], the choice of gauge is important. The true eigenvalue spectrum of V is continuous, and extends from $-\infty$ to ∞. Now, in the velocity gauge the eigenvalues of $\underline{V}$ are spread over a relatively narrow energy range, while in the length gauge they are spread over a wider range. Thus the low-energy portion of the spectrum of V is not covered so well in the length gauge. Furthermore, the larger eigenvalues of V, which are more numerous in the length gauge, are of less physical importance, and only give rise to aggravating temporal oscillations. *We therefore work in the velocity gauge.* In this gauge, V commutes with the product of the parity operator P and the time-reversal operator T. We may therefore write $V = QV_{\text{sym}}Q^\dagger$, where $Q = (PT)^{1/2}$ and $V_{\text{sym}} = QVQ^\dagger$. Since T complex conjugates c numbers, so does $QQ^\dagger$, and therefore the matrix representation of V_{sym}, which we denote by $\underline{V}_{\text{sym}}$ on the orthonormalized basis, is symmetric. Furthermore, when θ vanishes, V is Hermitian, and therefore $\underline{V}_{\text{sym}}$ is both *real* and *symmetric*. Since $\underline{V}$ scales with θ as $e^{-i\theta}$, we need only diagonalize the real symmetric $\underline{V}_{\text{sym}}$, and this can be done

rapidly. To construct $\underline{V}_{\text{sym}}$ we first construct the matrix representation of the operator V on the nonorthogonal Sturmian basis; this matrix is very sparse. We then obtain $\underline{V}$, on the orthonormalized basis, by pre- and post-multiplying by $\tilde{\underline{R}}$ and $\underline{R}$, respectively. The matrix $\underline{V}$ can be immediately symmetrized to give $\underline{V}_{\text{sym}} \equiv \underline{Q}^\dagger\underline{V}\underline{Q}$, where $\underline{Q}$ is a complex *diagonal* matrix (representing $\overline{Q}$) whose diagonal entries are either 1 or i. Furthermore, by grouping the even and odd orbital angular momenta separately, we can arrange that the upper left and lower right quarters of $\underline{V}_{\text{sym}}$ consist entirely of zeroes (with the upper right quarter the transpose of the lower left). If $\underline{Y}_{\text{sym}}$ is the *real* matrix which diagonalizes the real $\underline{V}_{\text{sym}}$, we have $\underline{Y} = \underline{Q}\underline{Y}_{\text{sym}}$, where $\underline{Y}^\dagger\underline{Y} = \underline{Y}\,\underline{Y}^\dagger = 1$. Note that this $\underline{Y}$ diagonalizes $\underline{V}$ for arbitrary κ, since for $\theta \neq 0$ we simply multiply the elements of $\underline{D}_{\text{int}}$ by $e^{-i\theta}$. Finally, we note that the eigenvalue spectrum of $\underline{V}_{\text{sym}}$ is symmetric with respect to the interchange of positive and negative eigenvalues, and that when P acts on an eigenvector of V it produces another eigenvector of V corresponding to an equal and opposite eigenvalue; hence we need only calculate *half* of the eigenvalues and eigenvectors of $\underline{V}_{\text{sym}}$. Summarizing, due to the structure of $\underline{V}_{\text{sym}}$, we can express $\underline{Y}_{\text{sym}}$ as

$$\underline{Y}_{\text{sym}} = \begin{pmatrix} \underline{B}_+ & \underline{B}_+ \\ \underline{B}_- & -\underline{B}_- \end{pmatrix} \;, \tag{12}$$

where $\underline{B}_\pm$ are real matrices whose row and column dimensions are $l_\pm n_{\text{rad}}$ and $(l_+ + l_-)n_{\text{rad}}/2$, respectively, where n_{rad} is the number of radial basis functions per orbital angular momentum quantum number l (we have taken n_{rad} to be independent of l) and where l_+ and l_- are, respectively, the maximum numbers of even and odd l. Hence we need not store the full $\underline{Y}$—we need only store the *real* matrices $\underline{B}_+$ and $\underline{B}_-$, each of whose dimensions are roughly *half* those of $\underline{Y}$. The structure of $\underline{Y}_{\text{sym}}$ is exploited in carrying out matrix multiplications with $\underline{Y}$ and $\underline{Y}^{-1}$.

III. TEST RESULTS

We show results for both ionization rates and yields. Before reporting our results for the rates, we describe how we extract a rate. To the extent that an ionization rate is meaningful, the system may be described by a single Floquet (dressed) state vector, with a quasienergy $E(I)$ which depends parametrically on the intensity profile $I(t)$. Let $\mathbf{v}(t)$ denote the state vector of the atom on our orthonormalized basis, and suppose that the field is monochromatic, with frequency ω. We have

$$\mathbf{v}(t) = \exp\left(-\frac{i}{\hbar}\int^t dt' \, E(I')\right)\mathbf{u}(t) \;, \tag{13}$$

where $\mathbf{u}(t)$ is approximately periodic in t (with period $2\pi/\omega$). Writing

$$E(I) = E_0 + \Delta(I) - i\Gamma(I)/2 \;, \tag{14}$$

where E_0 is the unperturbed initial energy level, we can calculate the width $\Gamma(I)$ and the shift $\Delta(I)$ (modulo $2\hbar\omega$)

[15], by evaluating the ratio $\tilde{\mathbf{v}}(\bar{t})\mathbf{v}(\bar{t})/\tilde{\mathbf{v}}(t)\mathbf{v}(t)$, where the tilde denotes the transpose, and where t and $\bar{t}$ are two times that differ by one period $2\pi/\omega$; with $\bar{t}$ the larger time, this ratio is approximately $e^{-2iE(I)(2\pi/\hbar\omega)}$. Note that in calculating $\tilde{\mathbf{v}}(t)\mathbf{v}(t)$ we encounter the matrix $\underline{\tilde{Y}}\,\underline{Y} \equiv \underline{\tilde{Y}}_{\mathrm{sym}}\underline{\tilde{Q}}\,\underline{Q}\underline{Y}_{\mathrm{sym}}$, but this consists only of the identity matrix in the upper right and lower left quarters, and the null matrix in the other two quarters.

All of our calculations were carried out for linear polarization. In Table I we present estimates of the rate for multiphoton ionization of H($1s$) at some different frequencies and intensities. In obtaining the results of Table I we took the temporal profile $I(t)$ of the intensity to be $I(t) = I_0 e^{-(t/t_{\mathrm{p}})^2}$ for $t \leq 0$ and $I(t) = I_0$ for $t \geq 0$, with $2\sqrt{\ln(2)}t_{\mathrm{p}}$, the full width at half maximum (FWHM) of the Gaussian, equal to seven cycles. Typically, we began the propagation at $t = -20$ cycles, and, from $t = 0$, we propagated for 30 cycles at the constant intensity I_0 (a total of 50 cycles). In Table I we compare our estimates

TABLE I. Rate Γ (in Hz) for ionization of H($1s$) by a field of intensity I_0 (in W/cm^2) and frequency ω (in a.u.). The rates are thoses calculated by (a) Chu and Cooper (Ref. [13]) (Floquet method); (b) present authors; and (c) Kulander (Ref. [9]). The notation $a[b]$ means $a \times 10^b$.

ω	I_0	Γ^{a}	Γ^{b}	Γ^{c}
0.55	7.00[12]	1.43[13]	1.43[13]	1.4[13]
0.28	7.00[12]	3.73[11]	4.0[11]	3.3[11]
0.28	4.38[13]	1.33[13]	1.35[13]	1.2[13]
0.20	4.38[13]	3.86[12]	4.0[12]	2.8[12]
0.20	1.75[14]	2.89[14]	2.7[14]	4.0[14]
0.20	3.94[14]	5.64[14]	6.0[14]	7.0[14]

with those obtained by Chu and Cooper [12] using the Floquet method, and those obtained by Kulander [11], who also extracted rates from the numerical integration of the time-dependent Schrödinger equation. Our results
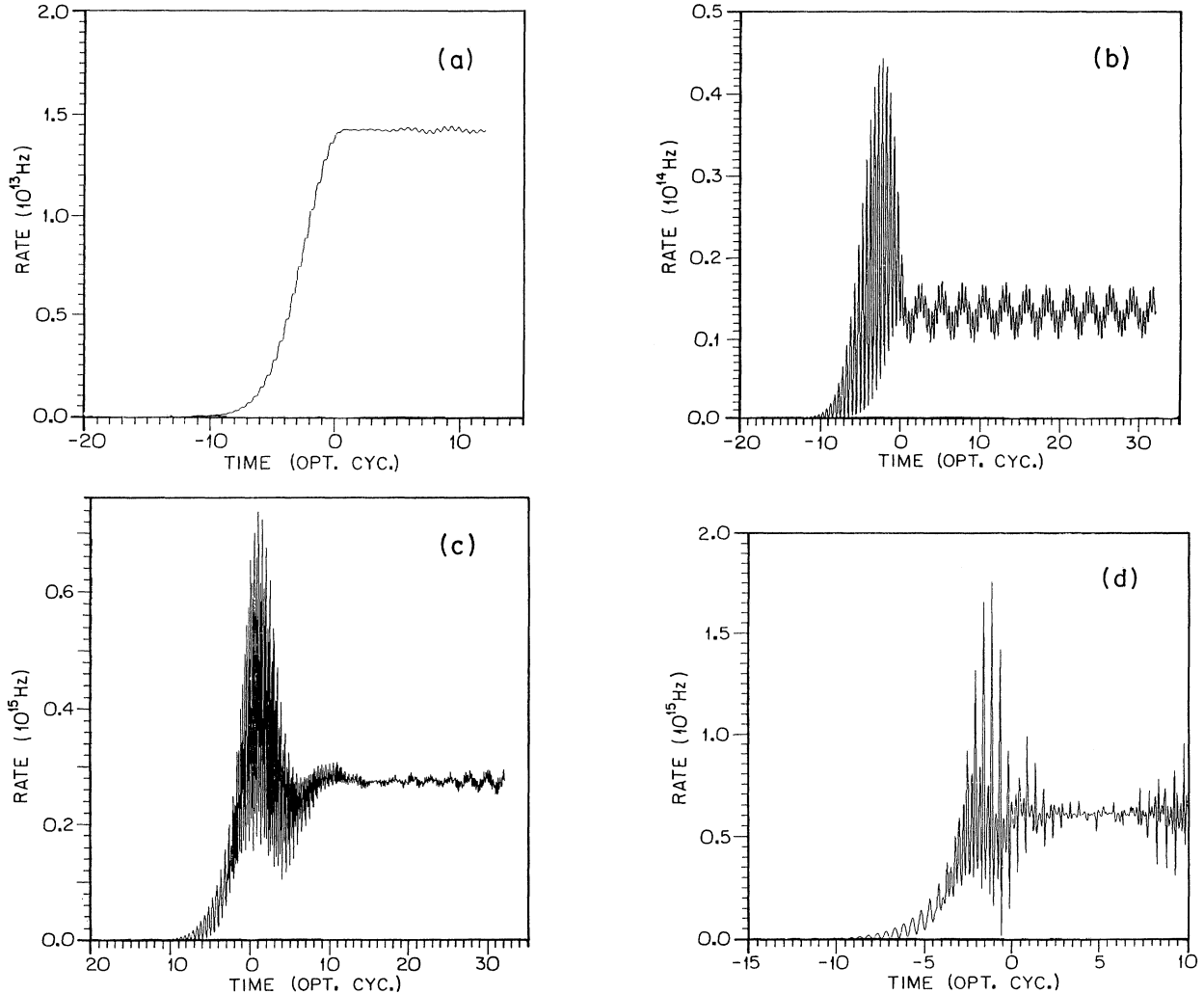

FIG. 1. Rate for ionization of H($1s$) vs time for a pulse whose intensity profile is $I(t) = I_0 e^{-(t/t_{\mathrm{p}})^2}$ when $t \leq 0$ and $I(t) = I_0$ when $t \geq 0$. The peak intensity I_0 (in W/cm^2) and frequency ω (in a.u.) are (a) $\omega = 0.55$, $I_0 = 7 \times 10^{12}$; (b) $\omega = 0.28$, $I_0 = 4.38 \times 10^{13}$; (c) $\omega = 0.20$, $I_0 = 1.75 \times 10^{14}$; (d) $\omega = 0.20$, $I_0 = 3.94 \times 10^{14}$.

are in reasonable agreement with those of Kulander, and in remarkably good agreement with Chu and Cooper. We must point out that our estimates of the rates given in Table I have been time averaged over the interval $t \geq 0$, when $I(t)$ is constant. The rates, calculated according to the prescription in the preceding paragraph, fluctuate with time. This is illustrated in Fig. 1 for some of the cases shown in Table I. The fluctuations, which are most pronounced during the rise of the pulse, have more than one source. There are numerous time scales, for example, those set by the bandwidth (the inverse rise time), the atomic orbital motion, the detuning from a resonance, the transit through a resonance, Rabi flopping, and the spreading of the electron wave packet. At very large times, the oscillations begin to grow, most probably due to the fact that the bound-state population of the atom is almost entirely depleted and nonexponential time behavior dominates. During the rise time of the pulse, more than one Floquet state may be populated if the intensity sweeps through a resonance. However, for the cases considered in producing Table I, the populations of the (dressed) excited states remain small—the Rabi flopping time (the inverse flopping frequency) is large compared to the transit time through a resonance (recall the rise time is only 20 cycles) and so the passage through a resonance is, by and large, diabatic. Furthermore, whatever population does go into a dressed excited state is rapidly transferred to the continuum. For example, when $\omega = 0.2$ a.u. there is a two-photon $1s$-$2s$ resonance [16] at an intensity not far below 1.75×10^{14} W/cm^2, but at this intensity the $1s$-$2s$ Rabi flopping time is many cycles, while the rate for ionization from the dressed $2s$ state is about three times larger than the rate for ionization from the dressed $1s$ state.

The results presented in Table I were obtained by using a basis set consisting of 31 radial functions per orbital angular momentum l, with $l \leq 5$. We took 400 time steps per cycle. Our computations required only 340 Kb of (core) storage and were carried out on a SUN-4/60 workstation with 8 Mb of CPU memory. The CPU time was about 2.5 min per cycle. We checked convergence by increasing the basis size and the number of time steps, and we encountered no difficulties due to reflection.

In Fig. 2 we show the probabilities for ionization of the $3s$ and $4s$ states of atomic hydrogen versus the peak intensity I_0 of a Gaussian pulse $I(t) = I_0 e^{-(t/t_{\rm P})^2}$ (all t) whose frequency is 0.2 a.u. and whose duration is held fixed. We have chosen the FWHM of the pulse to be five cycles (with the total duration 35 cycles). The ionization probability is evaluated at the end of the pulse, and is the difference from unity of the sum of the populations of all the bound states. As the intensity increases, the ionization probability at first increases, but it exhibits a maximum and a slow decrease as the peak intensity increases further. This "stabilization" of the atom against ionization at very high intensities, and frequencies above the threshold for one-photon ionization, has been predicted by numerous theorists [3]. It has also been predicted [17] that stabilization commences at an intensity at which the ponderomotive shift $P \equiv 2\pi I_0/(c\omega^2)$ is approximately equal to the photon energy ω; when $\omega = 0.2$
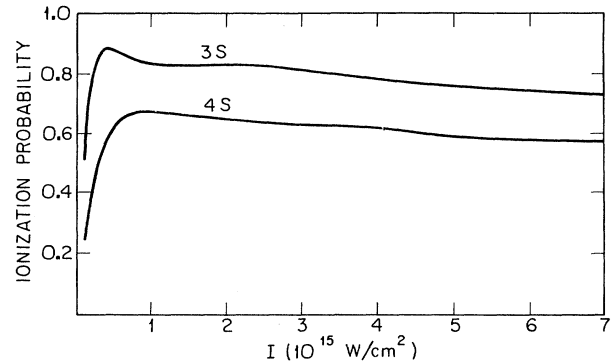

FIG. 2. Ionization probability vs the peak intensity of a Gaussian pulse of frequency 0.2 a.u. and a full width at half maximum of five cycles, for atomic hydrogen initially in the $3s$ or $4s$ state.

a.u., the ponderomotive and photon energies are equal at $I_0 \approx 1 \times 10^{15}$ W/cm^2, which is in the vicinity of the maxima of the yields of Fig. 2. Incidentally, for these five-cycle pulses, the frequency bandwidth is so large, and the peak intensity so high, that more than one Floquet state is appreciably populated, and it no longer makes sense to speak of a single rate for ionization.

We have also studied the yield for ionization of H($1s$) by a *bichromatic* radiation field, that is, by a superposition of two vector potentials $A_H(t) \cos(\omega_H t)$ and $A_L(t) \cos(\omega_L t + \phi_L)$, whose individual intensities have Gaussian profiles (both peaking at $t=0$). In Fig. 3 we show results in the case where one field has frequency $\omega_L = 0.099$ a.u., peak intensity 3×10^{13} W/cm^2, and a FWHM of seven low-frequency cycles, while the other field is the third harmonic, with frequency $\omega_H = 0.297$
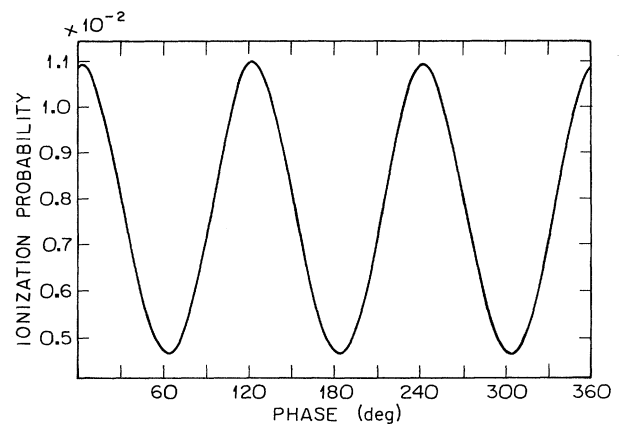

FIG. 3. Probability for ionization of H($1s$) by a bichromatic field, of frequencies 0.099 and 3×0.099 a.u., vs the phase of the fundamental field. The durations and peak intensities of the (Gaussian) pulses are given in the text.

a.u., peak intensity 1×10^{12} W/cm^2, and a FWHM of 15 high-frequency (that is, five low-frequency) cycles. In the absence of the high-frequency field, the low-frequency field cannot significantly ionize the atom, since at least six photons must be absorbed, but ionization via the simultaneous absorption of one high-frequency photon and several low-frequency photons is quite probable. We see, from Fig. 3, that the photoelectron yield oscillates with the phase ϕ_L of the fundamental and apparently this oscillation is periodic, with period equal to $2\pi/3$. The dependence of the yield on the relative phase between two fields with commensurable frequencies has been observed in the experiment by Muller et al. [4]. In general, if the ratio of the high frequency to the low frequency is p/q, the yield has an approximate periodicity of $2q\pi/p$ in the phase ϕ_L of the low-frequency field. This may be understood provided that an ionization rate (averaged over the fundamental cycle) is meaningful: A change of phase of $2q\pi/p$ in the low-frequency field may be compensated for by a shift in the origin of time by $2\pi/\omega_H$; the net field does not change under this combined transformation, as long as the relative intensities of the two fields may be treated as constant over the time interval $2\pi/\omega_H$, and hence the (Floquet) rate is periodic in ϕ_L [18].

IV. CONCLUSION

Our application to multiphoton ionization of atomic hydrogen indicates that if the full Hamiltonian is split into the atomic Hamiltonian and the atom-field interaction, the use of the split-operator technique in conjunction with a complex basis set is a promising method, at least for calculations of total ionization rates and level populations. The results presented here illustrate several points. First, provided that only time-averaged information is required, the Floquet method is applicable even for moderately short, moderately intense, pulses. Second, the stabilization of an atom against ionization should be an observable effect, but the frequency must be chosen to be several times larger than the threshold frequency for one-photon ionization so that the maximum ionization probability (which occurs at roughly the intensity for which the ponderomotive shift is equal to the photon energy) is still small; this is in agreement with the results of Floquet calculations [3,17]. Of course, the peak intensity of the pulse must be sufficiently high that stabilization occurs over a significant volume of atoms (spatial averaging inhibits stabilization since most atoms experience an intensity below the peak intensity at the focal center). Third, our results confirm that two-color ionization by a field and one of its harmonics can be very sensitive to the phase. We hope to report results for photoelectron energy spectra in a future paper.

ACKNOWLEDGMENTS

[1] See, e.g., K. C. Kulander, Phys. Rev. A **35**, 445 (1987); L. A. Collins and A. L. Merts, ibid. **40**, 4127 (1989); K. J. LaGattuta, ibid. **41**, 5110 (1990); X. Tang, H. Rudolph, and P. Lambropoulos, Phys. Rev. Lett. **65**, 3269 (1990); M. S. Pindzola and M. Dörr, Phys. Rev. A **43**, 439 (1991); J. Revai, Z. Phys. **16**, 129 (1990). For a more complete list of references, see the special issues of J. Opt. Soc. Am. B **7**, 407 (1990), edited by K. Kulander and A. L'Huillier; and Comput. Phys. Commun. **63**, 1 (1991), edited by K. Kulander.

[2] See, e.g., K. Schafer and K. C. Kulander, Phys. Rev. A **42**, 5798 (1990).

[3] See, e.g., M. Pont and M. Gavrila, Phys. Rev. Lett. **65**, 2362 (1990); P. Marte and P. Zoller, Phys. Rev. A **43**, 1512 (1991); Q. Su, J. H. Eberly, and J. Javanainen, Phys. Rev. Lett. **64**, 862 (1990); M. Dörr, R. M. Potvliege, and R. Shakeshaft, ibid. **64**, 2003 (1990); K. C. Kulander, K. J. Schafer, and J. L. Krause, ibid. **66**, 2601 (1991).

[4] H. Muller, P. H. Bucksbaum, D. W. Shuhmacher, and A. Zavriyev, J. Phys. B **23**, 2761 (1990); L. Pan and C. W. Clark (unpublished).

[5] M. Rotenberg, Adv. At. Mol. Phys. **6**, 233 (1970).

[6] A (real) Sturmian basis was first used in the numerical integration of the time-dependent Schrödinger equation for proton-hydrogen atom scattering by D. F. Gallaher and L. Wilets, Phys. Rev. **169**, 139 (1968); and subsequently by R. Shakeshaft, Phys. Rev. A **18**, 1930 (1978); and (for proton-helium atom scattering) T. G. Winter, ibid. **35**, 3799 (1987).

[7] R. M. Potvliege and R. Shakeshaft, Phys. Rev. A **38**, 1098 (1988); S.-I. Chu, K. Wang, and E. Layton, J. Opt. Soc. Am. B **7**, 425 (1990).

[8] Complex basis functions have been used previously to minimize reflections in time propagation. See W. P. Reinhardt, Annu. Rev. Phys. Chem. **33**, 223 (1982); C. W. McCurdy and S. D. Parker, Chem. Phys. Lett. **156**, 483 (1989); and C. W. McCurdy and C. K. Stroud, Comput. Phys. Commun. **63**, 323 (1991).

[9] For a discussion of the split-operator method, see M. J. Feit, J. A. Fleck, and A. Steiger, J. Comput. Phys. **47**, 412 (1982).

[10] Although at first sight the factorization of the time dependence might seem to be a unique feature of the atom-radiation system, this is not so; the time-dependent Schrödinger equation for colliding atoms or ions can be transformed into a form in which a scaled time dependence also appears only in c-number factors of the (transformed) interactions. See E. A. Solov'ev, Usp. Fiz. Nauk **157**, 437 (1989) [Sov. Phys.—Usp. **32**, 228 (1989)].

[11] K. C. Kulander, Phys. Rev. A **35**, 445 (1987),

[12] S.-I. Chu and J. Cooper, Phys. Rev. A **32**, 2769 (1985).

[13] Although $\underline{Y}$ appears without $\underline{X}$ at the end points of the interval $[t_0, t_N]$, we project onto eigenvectors of $\underline{X}$ and we

may therefore replace $\underline{Y}^{-1}$ by $\underline{Y}^{-1}\underline{X}$ at the end points.

[14] The problem of reflection of the photoelectron wave at boundaries in position space may also be avoided by working in momentum space. See, for example, M. Dörr and R. Shakeshaft, Phys. Rev. A **38**, 543 (1988) for an application to a one-dimensional model, and L. A. Collins and A. L. Merts, J. Opt. Soc. Am. B **7**, 647 (1990) for an application to a three-dimensional model. The basis consists of the "Volkov" state vectors which describe an electron moving freely through the oscillating field. Unitarity is preserved, and the photoelectron energy spectrum may be obtained straightforwardly. However, working in momentum space introduces other problems—in particular, the atomic potential is nonlocal—and so far as we are aware no calculations for a real atom have been carried out in momentum space.

[15] To calculate the shift modulo $\hbar\omega$ (rather than $2\hbar\omega$) we may evaluate the ratio $\tilde{v}(\bar{t})v(t)/\hat{v}(t)v(t)$.

[16] R. Shakeshaft and X. Tang, Phys. Rev. A **36**, 3193 (1987).

[17] M. Dörr, R. M. Potvliege, D. Proulx, and R. Shakeshaft, Phys. Rev. A **43**, 3729 (1991).

[18] See also M. Dörr, R. M. Potvliege, D. Proulx, and R. Shakeshaft, Phys. Rev. A **44**, 574 (1991).