Ionization rates of H_2^+ in an intense laser field by numerical integration of the time-dependent Schrödinger equation

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A numerical method of integration of the time-dependent Schrödinger equation is presented for the hydrogen atom and for the H_2^+ molecule. Cylindrical coordinates are used and the wave function is expressed as a Bessel-Fourier series. This expansion allows one to eliminate singularities present in the Hamiltonian and to use a unitary split operator to evaluate numerically multiphoton transitions. Laser-induced ionization rates for H_2^+ are calculated and compared with rates for the hydrogen atom. A strong dependence of the H_2^+ ionization rates on the initial vibrational excitation is found.

The interaction of intense laser pulses (intensity $> 10^{13}$ W/cm^2) with atoms and molecules leads to many interesting multiphoton phenomena such as above-threshold ionization (ATI) and high-order harmonic generation. This has been an area of active research in the past decade and is well documented in several review papers [1–4]. The topic is a challenge for theoreticians since standard perturbation theories are not valid for intensities approaching the intensity atomic-unit value ($\cong 3.5 \times 10^{16}$ W/cm^2). In most existing theoretical models based on exact analytic solutions of the Schrödinger equation the laser field is represented as a monochromatic wave. Since in most experiments the electric-field amplitude can vary considerably on a scale of several cycles during the turn-on of the pulse, it is necessary to describe these high-intensity phenomena by solving numerically the time-dependent Schrödinger equation (TDSE) on recently available powerful computers [5–15].

In this paper we introduce a numerical technique for integration of the TDSE which holds some promise for improving computational efficiency. The method is particularly attractive for problems exhibiting cylindrical symmetry such as the problem of linearly polarized light interacting with a H atom or a H_2^+ molecule, the molecule being collinear with the electric field. Calculations are performed in cylindrical coordinates (ρ, z, ϕ). The transverse variable ρ is eliminated with the help of the Bessel-Fourier series [16–18]. This allows us to eliminate the singularities present in the Laplacian and in the potential in order to use a split-operator technique together with fast Fourier transform (FFT) [19–21]. It is well known that this method allows one to use larger time and space steps than the finite-difference methods and is particularly useful for problems with short-range potentials [19,20]. Similar techniques for problems in which Coulomb potentials are present were already used previously but with different basis sets or different coordinates in Refs. [14,21]. Elimination of the ρ variable with the help of the Bessel-Fourier expansion yields a set of differential equations (with variables t and z only) with no singularity at

$z = 0$ and therefore techniques based on FFT will work better in this basis than with the commonly used expansion in spherical harmonics. The computational efficiency of the method is related to the fact that the wave function even at high intensities is well localized within a long and thin cylinder. The method is particularly well suited for the H_2^+ case for which expansion in spherical harmonics may not work so well as for atoms since already the ground state requires a considerable number of harmonics, which is expected to increase considerably during the interaction (absorption of photons).

We apply this technique for the case of the interaction of a laser pulse with a hydrogen molecule ion H_2^+. We calculate the ionization rates for the H_2^+ and compare with rates for the H atom. We are motivated by the fact that there is general interest in resonant dissociation of H_2^+ by an intense laser pulse [22–24]. This process is typically described by a model in which only the ground electronic surface and the first repulsive surface are included [22,24] (i.e., ionization and upper electronic surfaces are neglected). Therefore it is important to know up to what intensities predictions of this model are correct. One of the predictions by the two-electronic-state model is the very interesting phenomenon of laser-induced molecular stabilization with respect to the dissociation at high laser intensities. We wish to examine to what extent the ionization may affect this stabilization.

In cylindrical coordinates and in atomic units the TDSE describing the interaction of matter with linearly polarized laser field has the following form (the z axis is chosen along the electric-field E direction):

$$i\frac{\partial \psi}{\partial t} = -\frac{1}{2}\frac{\partial^2 \psi}{\partial z^2} + D_\rho \psi + V_C(\rho, z)\psi + ezE(t)\psi, \quad (1)$$

where

$$D_\rho = -\frac{1}{2}\frac{\partial^2}{\partial \rho^2} - \frac{1}{2\rho}\frac{\partial}{\partial \rho}, \quad (2)$$

$$V_C(\rho,z) = \begin{cases} -(\rho^2+z^2)^{-1/2}, & \text{for H}, \\ -[\rho^2+(z-R/2)^2]^{-1/2}-[\rho^2+(z+R/2)^2]^{-1/2}, & \text{for } H_2^+, \end{cases} \tag{3}$$

and R is the internuclear separation of H_2^+. In the calculations we assumed R to be fixed and equal to either 2.0 a.u. (H_2^+ in the ground state) or to 3.0 a.u. (H_2^+ in an excited vibrational state). Note that there are no terms depending on angle ϕ in (1). These terms can be omitted due to the symmetry of this problem (the potentials and wave function at $t=0$ do not depend on ϕ) [5]. Numerical integration of Eq. (1) using a finite-difference scheme requires special care near $\rho=0$ because of the singularity in D_ρ and in the potential $V_C(\rho,z)$ (usually smaller space steps are required near a singularity). We propose here to use the Bessel-Fourier series built from the functions [16–18]

$$v_n(\rho) = \frac{2^{1/2}}{LJ_1(x_n)}J_0(x_n\rho/L), \tag{4}$$

where J_0 and J_1 are Bessel functions, x_n are zeros of $J_0(x)$ and L is the maximal value of ρ used in our calculations. If the wave function is expanded in this series the singularity $1/\rho$ present in D_ρ can be removed since the functions $v_n(\rho)$ are eigenfunctions of this operator; i.e., we have

$$D_\rho v_n(\rho) = -(x_n/L)^2 v_n(\rho). \tag{5}$$

The series of functions $v_n(\rho)$ constitutes a complete basis for functions $f(\rho)$ defined on the interval $(0,L)$ having continuous second derivatives at the origin $(\rho=0)$ and satisfying the condition $f(L)=0$ [18]. These functions form an orthonormal set of functions satisfying the relations

$$\int_0^L v_n(\rho)v_m(\rho)\rho d\rho = \delta_{n,m}. \tag{6}$$

Thus after expanding the wave function in this basis according to the formula

$$\psi(\rho,z,t) = \sum_{n=1}^M \phi_n(z,t)v_n(\rho), \tag{7}$$

inserting it into the Schrödinger equation (1), and eliminating the ρ variable with the help of Eq. (6) one gets the following system of partial differential equations in z and t only:

$$i\frac{\partial}{\partial t}\phi = -\frac{1}{2}\frac{\partial^2}{\partial z^2}\phi + A(z)\phi + eE(t)z\phi, \tag{8}$$

where $\phi = \phi(z,t)$ is a vector containing $\phi_n(z,t)$ defined by (7) and $A(z)$ is a $M \times M$ matrix with its elements defined by the formula:

$$A_{n,k}(z) = \tfrac{1}{2}(x_n/L)^2\delta_{n,k} + \int_0^L v_n(\rho)V_C(\rho,z)v_k(\rho)\rho d\rho \tag{9}$$

[note that the matrix potential $A(z)$ which replaces the Coulomb potential is nonsingular at $z=0$].

This system of differential equations (8) is integrated using the second-order split-operator technique [19–21], i.e., the time-evolution algorithm is based on the relation

$$\phi(t+\delta t,z) = \exp(D_z\delta t)\exp[-iE(t')z\delta t]$$

$$\times \exp[-iA(z)\delta t]\exp(D_z\delta t)\phi(t,z), \tag{10}$$

where $D_z = (i/4)\partial^2/\partial z^2$ and $t'=t+\delta t/2$. The operation $\exp(D_z\delta t)\phi$ is performed with the help of FFT and the matrix $B(z)=\exp[-iA(z)\delta t]$ was evaluated using the formula (valid for any Hermitian matrix A)

$$B = U\exp(-iA_D\delta t)U^T, \tag{11}$$

where U is the diagonalizing matrix (it contains eigenvectors of the matrix A as its columns) and A_D is the diagonalized matrix A. The matrix $\exp(-iA_D\delta t)$ is simply a diagonal matrix containing the exponentials of the eigenvalues of A. Calculation of the matrix B for each z is time consuming but needs to be done only once since B is time independent. The propagation scheme (10) is always unitary.

We calculated first the population of the ground state $P_{1s}(t) = |\langle\psi_{1s}|\psi(t)\rangle|^2$ of the hydrogen atom and obtained full agreement with the published data [13] using only $M=16$ functions in the expansion in Bessel functions which shows that the technique is quite efficient. The Schrödinger equation (1) for H_2^+ was then integrated numerically using the ground-state wave function of H_2^+ $\psi_0(z,R)$, given in Ref. [25] (exact eigenfunction obtained in parabolic coordinates, taken from the Table II-A of Ref. [25]), as an initial condition. The size of the grid was defined by $|z| < 128$ a.u., the spatial integration step Δz was $\tfrac{1}{8}$ a.u., $L=8$ a.u., and the time step δt was 0.01 a.u. The electric field was described by the formula $E(t) = E_0U(t)\sin(\omega t)$ where $U(t)=1$ for $t > t_0$, $U(t)=t/t_0$ for $0 < t < t_0$, $\omega=0.2$ a.u., $t_0=5$ cycles $\cong 157$ a.u., and E_0 is the laser peak electric field in atomic units.

Typically the ground-state population $P_0(t) = |\langle\psi_0|\psi(t)\rangle|^2$ is an exponential-like function from which the ionization rate λ can be calculated as $-\ln[P_0(t)]$. This formula cannot be used when resonant phenomena
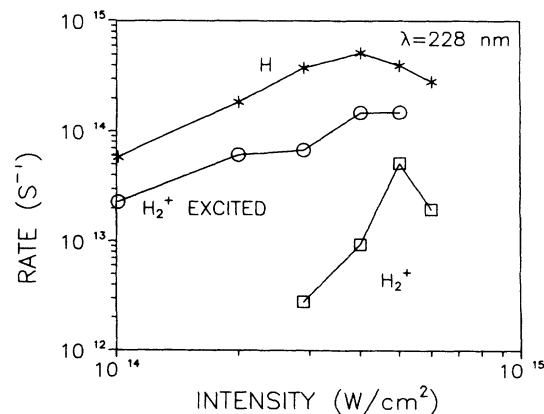

FIG. 1. Ionization rates as functions of laser intensity for the hydrogen atom $(\times)$, for H_2^+ in equilibrium position $(R=2$ a.u.) $(\square)$, and for H_2^+ with $R=3$ a.u. $(\bigcirc)$.
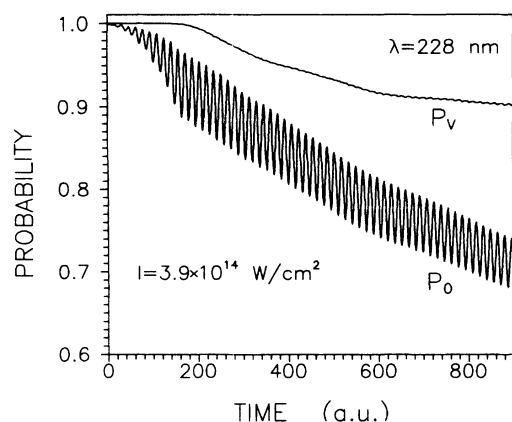
FIG. 2. Time dependence of the population of the ground state P_0 and of the function P_V at intensity 3.94×10^{14} W/cm^2 for $R = 2$ a.u. (equilibrium separation).

FIG. 3. Same as in Fig. 2 but for $R = 3$ a.u.

take place. Therefore we define the ionization rate in a similar way as in Ref. [13], i.e., we apply a best exponential fit to the function

$$P_V(t) = \int_{-z_M}^{z_M} dz \int_0^L d\rho\, \rho |\psi|^2 , \qquad (12)$$

which represents the probability of finding the electron in a cylinder in which many bound states are contained. For our purposes, we found to be sufficient $z_M = 16$ a.u. The ionization rates as functions of laser intensity are displayed in Fig. 1. The time dependence of the ground-state population $P_0(t)$ and of the function $P_V(t)$ for an intensity $I = 4 \times 10^{14}$ W/cm^2, for $R = 2$ a.u. (the equilibrium separation) and for $R = 3$ a.u. are shown in Figs. 2 and 3, correspondingly. We observe a big difference (more than 2 orders of magnitude) between the rates of H and those of H$_2^+$ ($R = 2$ a.u.) for intensities below 4×10^{14} W/cm^2 and nuclei at the equilibrium position. However, we see a dramatic increase of the ionization rate of H$_2^+$ when the internuclear separation R is 3 a.u. (which roughly corresponds to the fourth excited vibrational state). This strong dependence of the rate on the internuclear separation is related to the very steep decrease of the H$_2^+$ repulsive surface σ_u as function of R [26]. For R equal to the equilibrium separation ($R = 2$ a.u.) one needs approximately two photons to reach the upper surface while for $R = 3$ a.u. one already is at one-photon resonance. (Thus at the present wavelength, $\lambda = 228$ nm, the right-hand turning point of the $v = 3$ level is degenerate, in the dressed-molecule picture, with the nuclear turning point on the repulsive surface [24].) This largely enhances the ionization since in the upper repulsive (antibonding) surface σ_u the probability for the electron to stay between the nuclei (where the attraction from nuclei is the strongest) becomes small (by symmetry) compared to that of the bonding ground state [26]. The resonant behavior for this case is seen in Fig. 3. One clearly sees the Rabi oscil-
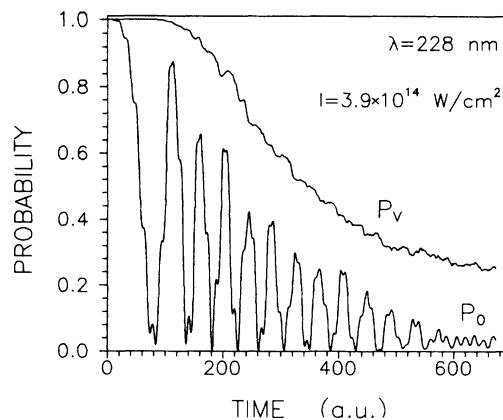
lations of P_0. Obviously for this case the rate must be calculated from P_V instead of P_0.

In all our calculations the grid size was defined by the inequality $|z| < 128$ a.u. In order to check whether our results are affected by the reflections from the boundary we repeated the calculation using the absorbing-mask function introduced in Ref. [15]. We observed a considerable absorption when the ground-state population P_0 is largely depleted. However, this had little influence on the ionization rates calculated from either the P_0 or P_V functions.

In conclusion, we note that at intensities above 10^{13} W/cm^2 for which the ionization rates exceed 2×10^{13} s^{-1} the molecular stability with respect to the dissociation may be affected by the ionization (at $I = 10^{14}$ W/cm^2 we observed ionization probability equal to 0.2 at $t = 10$ fs). We also note that ionization rate is strongly dependent on the initial vibrational excitation. In the present calculations the internuclear distance was kept fixed and the kinetic energy of nuclei omitted. It is plausible to think that at the high intensities considered here the ionization process is occurring so fast ($\tau_i \cong 10^{-15}$ s) that the calculation in which the nuclei are frozen gives a reasonable estimate of the ionization rate. A complete study of the effect of nuclear motion on ionization rates, as well as the harmonic generation by H$_2^+$ will be presented in a further paper. Harmonic generation by a neutral hydrogen molecule was recently discussed in Ref. [27] and compared with that by atomic hydrogen. The authors observed little molecular effects, i.e., their H$_2$ results were similar to their hydrogen results. For the H$_2^+$ and for frequencies close to resonance we expect to encounter more molecular vibrational effects in harmonic generation in our calculations.

[1] J. H. Eberly, J. Javanainen, and K. Rzazewski, Phys. Rep. **204**, 331 (1991).

[2] G. Mainfray and C. Manus, Rep. Prog. Phys. **54**, 1333 (1991).

[3] A. L'Huillier, K. J. Schafer, and K. C. Kulander, J. Phys. B **24**, 3315 (1991).

[4] M. V. Fedorov and A. E. Kazakov, Prog. Quantum Electron. **13**, 1 (1989); N. B. Delone and M. Fedorov, *ibid.* **13**, 267 (1989).

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

[6] J. H. Eberly, Q. Su, and J. Javanainen, Phys. Rev. Lett. **62**, 881 (1989).

[7] J. H. Eberly, Q. Su, and J. Javanainen, J. Opt. Soc. Am. B **6**, 1289 (1989).

[8] K. C. Kulander and B. W. Shore, Phys. Rev. Lett. **62**, 524 (1989).

[9] K. C. Kulander and B. W. Shore, J. Opt. Soc. Am. B **7**, 502 (1990).

[10] P. L. DeVries, J. Opt. Soc. Am. B **7**, 517 (1990).

[11] K. C. Kulander, K. J. Schafer, and J. L. Krause, Phys. Rev. Lett. **66**, 2601 (1991).

[12] K. LaGattuta, Phys. Rev. A **43**, 5157 (1991).

[13] K. LaGattuta, Phys. Rev. A **41**, 5110 (1990).

[14] M. Pont, D. Proulx, and R. Shakeshaft, Phys. Rev. A **44**, 4486 (1991).

[15] J. L. Krause, K. J. Schafer, and K. C. Kulander, Phys. Rev. A **45**, 4998 (1992).

[16] J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1962), p. 429.

[17] W. Kaplan, *Advanced Calculus* (Addison-Wesley, Reading, MA, 1952).

[18] G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge Univ. Press, Cambridge, 1966), p. 576.

[19] M. D. Feit, J. A. Fleck, Jr., and A. Steiger, J. Comput. Phys. **47**, 412 (1982); M. D. Feit and J. A. Fleck, Jr., J. Chem. Phys. **78**, 2578 (1984); J. N. Bardsley, A. Szöke, and J. M. Comella, J. Phys. B **21**, 3899 (1988); H. Kono and S. H. Lin, J. Chem. Phys. **84**, 1071 (1986).

[20] A. D. Bandrauk and H. Shen, Chem. Phys. Lett. **176**, 428 (1991).

[21] M. R. Hermann and J. A. Fleck, Phys. Rev. A **38**, 6000 (1988).

[22] A. D. Bandrauk and M. L. Sink, Chem. Phys. Lett. **57**, 569 (1978); J. Chem. Phys. **74**, 1110 (1981).

[23] P. H. Bucksbaum, A. Zariyev, H. G. Muller, and D. W. Schumacher, Phys. Rev. Lett. **64**, 1883 (1990); Phys. Rev. A **42**, 5500 (1990); J. W. J. Verschuur, L. D. Nordham, and H. B. van Linden van den Heuvel, Phys. Rev. A **40**, 4383 (1989); S. W. Allendorf and A. Szöke, Phys. Rev. A **44**, 518 (1991).

[24] A. D. Bandrauk, E. Constant, and J. M. Gauthier, J. Phys. II (France) **1**, 1033 (1991).

[25] E. Teller and H. L. Sahlin, in *Physical Chemistry, an Advanced Treatise,* edited by H. Eyring (Academic, New York, 1970), Vol. V.

[26] I. N. Levine, *Quantum Chemistry* (Allyn and Bacon, Boston, 1983), p. 328.

[27] J. L. Krause, K. J. Schafer, and K. C. Kulander, Chem. Phys. Lett. **178**, 573 (1991).