

## Multiphoton ionization of $H_2^+$

Moon-Gu Baik, Marcel Pont, and Robin Shakeshaft

*Physics Department, University of Southern California, Los Angeles, California 90089-0484*

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We present results of calculations of rates for ionization of  $H_2^+$  by up to six photons in lowest nonvanishing order of perturbation theory, for a fixed internuclear separation of 2 a.u. There are numerous intermediate state resonances, which we identify by united-atom-limit quantum numbers. We also report on ionization rates at nonperturbative intensities at the wavelength 228 nm, calculated by resumming the Rayleigh-Schrödinger perturbation series for the ac quasienergy; we compare our results with those of previous calculations. [S1050-2947(96)04808-1]

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### I. INTRODUCTION

We have calculated, up to fairly high order, terms of the Rayleigh-Schrödinger perturbation series for the ac quasienergy of the lowest electronic state of the molecular ion  $H_2^+$  at a fixed internuclear separation. We report, in particular, on rates for ionization of  $H_2^+$  by up to six photons in lowest nonvanishing order of perturbation theory, for the equilibrium internuclear separation 2 a.u. We ignore vibrational and rotational motion, and we consider only one orientation of the molecule, the orientation along the polarization axis of the (linearly polarized) laser field. The ionization rates exhibit numerous resonances, as the frequency of the light is varied, and we identify those intermediate electronic states involved in the resonances by united-atom-limit quantum numbers. Some of the resonances are prominent at large detunings, while others are not, a feature that can be understood to some extent by looking at the overlap of the ground-state probability density, amplified by the  $(2n)$ th power of the electric dipole moment in the case of an  $n$ -photon resonance, with the probability density of the resonant state.

Recently Plummer and McCann [1] calculated rates for ionization of  $H_2^+$  by two and three photons within the nonperturbative Floquet framework, over the range of frequencies at which excess photon ionization does not occur when the laser field is weak. Our results for two- and three-photon ionization agree well with theirs at low (perturbative) intensities, over the entire range of frequencies considered. Chelkowski *et al.* [2] and Mies *et al.* [3] have also calculated rates for ionization of  $H_2^+$ ; they did so by solving the time-dependent Schrödinger equation at the wavelength 228 nm for various intensities extending well into the nonperturbative regime. We have resummed the Rayleigh-Schrödinger perturbation series at this wavelength, using the Padé method, and we compare our results for the ionization rate with those of Chelkowski *et al.* and Mies *et al.* at the intensities considered by them.

In the next section we describe how we calculate the Green's function for the electronic motion of  $H_2^+$ . The Green's function is needed for the evaluation of the terms of the perturbation series. We exploit the separability of the electronic Hamiltonian so as to significantly reduce the storage requirements and the number of computational opera-

tions. In Sec. III we present our results, and in Sec. IV we conclude with some remarks.

### II. THEORY

Following Bates and Opik [4], who studied one-photon ionization of  $H_2^+$ , and Plummer and McCann [1], we use prolate spheroidal coordinates  $(\lambda, \mu, \phi)$  to represent the electron, where  $\phi$  is the azimuthal angle (with the polar axis along the internuclear axis). If  $R$  is the internuclear separation, and if  $r_a$  and  $r_b$  are the distances of the electron from nuclei  $a$  and  $b$ , we have

$$\lambda = (r_a + r_b)/R, \quad (1)$$

$$\mu = (r_a - r_b)/R, \quad (2)$$

with  $1 \leq \lambda \leq \infty$  and  $-1 \leq \mu \leq 1$ . The electronic Hamiltonian is (we use atomic units throughout this section)

$$H = -\frac{1}{2}\nabla^2 - 2\frac{(Z_a + Z_b)\lambda - (Z_a - Z_b)\mu}{R(\lambda^2 - \mu^2)}, \quad (3)$$

where  $Z_a = Z_b = 1$  in the case of  $H_2^+$ , and where

$$\nabla^2 = \frac{4}{R^2(\lambda^2 - \mu^2)} \left[ \frac{\partial}{\partial \lambda} \left( (\lambda^2 - 1) \frac{\partial}{\partial \lambda} \right) + \frac{\partial}{\partial \mu} \left( (1 - \mu^2) \frac{\partial}{\partial \mu} \right) + \left( \frac{1}{(\lambda^2 - 1)} + \frac{1}{(1 - \mu^2)} \right) \frac{\partial^2}{\partial \phi^2} \right]. \quad (4)$$

We expand the electronic wave function on a basis composed of functions of the form

$$u_\nu(\lambda)v_\eta(\mu)\frac{e^{im\phi}}{\sqrt{2\pi}}.$$

Since the volume element is  $d\tau = (R/2)^3(\lambda^2 - \mu^2)d\lambda d\mu d\phi$ , the electronic Hamiltonian has the following simple product representation:

$$H_{\nu',\nu}^{\eta',\eta} = h_{\nu',\nu} \tilde{s}^{\eta',\eta} + h_{\nu',\nu}^{\eta',\eta} \tilde{s}_{\nu',\nu}, \quad (5)$$

where we have not included  $m$  as an index since  $H$  has cylindrical symmetry about the internuclear axis, and where the matrix elements on the right side are defined as

$$h_{\nu',\nu} = -\frac{R}{4} \int_1^\infty d\lambda u_{\nu'}(\lambda) \left( \frac{\partial}{\partial \lambda} (\lambda^2 - 1) \frac{\partial}{\partial \lambda} - \frac{m^2}{(\lambda^2 - 1)} \right) u_\nu(\lambda) + R(Z_a + Z_b)\lambda u_\nu(\lambda), \quad (6)$$

$$\tilde{s}_{\nu',\nu} = \int_1^\infty d\lambda u_{\nu'}(\lambda) u_\nu(\lambda), \quad (7)$$

$$h^{\eta',\eta} = -\frac{R}{4} \int_{-1}^1 d\mu v_{\eta'}(\mu) \left( \frac{\partial}{\partial \mu} (1 - \mu^2) \frac{\partial}{\partial \mu} - \frac{m^2}{(1 - \mu^2)} - R(Z_a - Z_b)\mu \right) v_\eta(\mu), \quad (8)$$

$$\tilde{s}^{\eta',\eta} = \int_{-1}^1 d\mu v_{\eta'}(\mu) v_\eta(\mu). \quad (9)$$

If  $\underline{H}$  denotes the electronic Hamiltonian matrix, whose elements are  $H_{\nu',\nu}^{\eta',\eta}$ , and if  $\underline{h}_\lambda$ ,  $\underline{h}^\mu$ ,  $\underline{s}_\lambda$ , and  $\underline{s}^\mu$ , respectively, denote the smaller matrices whose elements are  $h_{\nu',\nu}$ ,  $h^{\eta',\eta}$ ,  $\tilde{s}_{\nu',\nu}$ , and  $\tilde{s}^{\eta',\eta}$ , we can express  $\underline{H}$  as a sum of direct products:

$$\underline{H} = \underline{h}_\lambda \underline{s}^\mu + \underline{s}_\lambda \underline{h}^\mu. \quad (10)$$

The overlap matrix  $\underline{S}$  of the basis functions has elements  $S_{\nu',\nu}^{\eta',\eta}$ , where

$$S_{\nu',\nu}^{\eta',\eta} = s_{\nu',\nu} \tilde{s}^{\eta',\eta} + \tilde{s}_{\nu',\nu} s^{\eta',\eta}, \quad (11)$$

and where

$$s_{\nu',\nu} = (R/2)^3 \int_1^\infty d\lambda u_{\nu'}(\lambda) (\lambda^2 - 1) u_\nu(\lambda), \quad (12)$$

$$s^{\eta',\eta} = (R/2)^3 \int_{-1}^1 d\mu v_{\eta'}(\mu) (1 - \mu^2) v_\eta(\mu). \quad (13)$$

If  $\underline{s}_\lambda$  and  $\underline{s}^\mu$ , respectively, denote the smaller matrices whose elements are  $s_{\nu',\nu}$  and  $s^{\eta',\eta}$ , we have

$$\underline{S} = \underline{s}_\lambda \underline{s}^\mu + \underline{s}_\lambda \underline{s}^\mu. \quad (14)$$

The reduction of  $\underline{H}$  and  $\underline{S}$  to direct products of smaller matrices, a consequence of the separability of the Hamiltonian, leads to a significant savings in computational storage.

The Green's function  $G(E) \equiv (E - H)^{-1}$  is represented by the matrix  $(\underline{E}\underline{S} - \underline{H})^{-1}$ . To calculate rates for multiphoton ionization, we need to determine the action of the Green's function on a specified vector. Towards this end, we now consider the following two uncoupled generalized eigenvalue problems for eigenvalues  $\mathcal{E}_\alpha$  and  $\mathcal{E}^\beta$  and eigenvectors  $\mathbf{x}_\alpha$  and  $\mathbf{x}^\beta$ :

$$(\underline{E}\underline{s}_\lambda - \underline{h}_\lambda) \mathbf{x}_\alpha = \mathcal{E}_\alpha \underline{s}_\lambda \mathbf{x}_\alpha, \quad (15)$$

$$(\underline{E}\underline{s}^\mu - \underline{h}^\mu) \mathbf{x}^\beta = \mathcal{E}^\beta \underline{s}^\mu \mathbf{x}^\beta, \quad (16)$$

with the eigenvectors orthonormalized, that is,

$${}^t(\mathbf{x}_\alpha') \underline{s}_\lambda \mathbf{x}_\alpha = \delta_{\alpha',\alpha}, \quad (17)$$

$${}^t(\mathbf{x}^{\beta'}) \underline{s}^\mu \mathbf{x}^\beta = \delta_{\beta',\beta}, \quad (18)$$

where  $t$  denotes transpose. If  $\mathbf{x}_\alpha^\beta$  is the joint column vector that combines  $\mathbf{x}_\alpha$  and  $\mathbf{x}^\beta$ , we have

$$(\underline{E}\underline{S} - \underline{H}) \mathbf{x}_\alpha^\beta = [(\underline{E}\underline{s}_\lambda - \underline{h}_\lambda) \mathbf{x}_\alpha] (\underline{s}^\mu \mathbf{x}^\beta) + [(\underline{E}\underline{s}^\mu - \underline{h}^\mu) \mathbf{x}^\beta] (\underline{s}_\lambda \mathbf{x}_\alpha) \quad (19)$$

$$= (\mathcal{E}_\alpha + \mathcal{E}^\beta) (\underline{s}_\lambda \mathbf{x}_\alpha) (\underline{s}^\mu \mathbf{x}^\beta) \quad (20)$$

$$= (\mathcal{E}_\alpha + \mathcal{E}^\beta) \underline{s}_\lambda \underline{s}^\mu \mathbf{x}_\alpha^\beta. \quad (21)$$

Consequently, if  $x_\lambda$  and  $x^\mu$  are the matrices composed of all column vectors  $\mathbf{x}_\alpha$  and  $\mathbf{x}^\beta$ , respectively, if  $\underline{X} \equiv x_\lambda x^\mu$  and  $\underline{\tilde{S}} \equiv \underline{s}_\lambda \underline{s}^\mu$ , and if  $\underline{D}$  is the diagonal matrix whose diagonal elements are  $(\mathcal{E}_\alpha + \mathcal{E}^\beta)$ , we have

$$(\underline{E}\underline{S} - \underline{H}) \underline{X} = \underline{\tilde{S}} \underline{X} \underline{D}. \quad (22)$$

To calculate  $\mathbf{y} \equiv (\underline{E}\underline{S} - \underline{H})^{-1} \mathbf{b}$ , where  $\mathbf{b}$  is a specified vector, we must solve the set of linear equations

$$(\underline{E}\underline{S} - \underline{H}) \mathbf{y} = \mathbf{b}. \quad (23)$$

Writing  $\mathbf{y} = \underline{X} \mathbf{z}$  and combining Eqs. (22) and (23) gives

$$\underline{\tilde{S}} \underline{X} \underline{D} \mathbf{z} = \mathbf{b}. \quad (24)$$

From Eqs. (17) and (18) we have the orthogonality condition

$${}^t \underline{X} \underline{\tilde{S}} \underline{X} = \underline{1}, \quad (25)$$

where  $\underline{1}$  is the identity matrix. It follows that

$$\mathbf{y} = \underline{X} (\underline{D}^{-1}) {}^t \underline{X} \mathbf{b}. \quad (26)$$

Hence, to determine the action of the Greens function we need only solve the generalized eigenvalue problems for  $\underline{X}$  and  $\underline{D}$ , Eq. (22), and this is not difficult to do since Eqs. (15) and (16) are uncoupled so that the number of operations is reasonably small.

Let  $\mathbf{e}$  be the unit polarization vector,  $\omega$  the frequency, and  $F$  the field strength of the light. The interaction of the electron with the light is  $V_+ e^{-i\omega t} + V_- e^{i\omega t}$  where  $V_- = V_+^\dagger$  and where, in the length gauge,

$$V_+ = (F/2) \mathbf{e} \cdot \mathbf{x}, \quad (27)$$

where  $\mathbf{x}$  is the electron coordinate, while in the velocity gauge

$$V_+ = (F/2\omega) \mathbf{e} \cdot \nabla. \quad (28)$$

Writing  $\mathbf{x} = (x, y, z)$  we have

$$x = (R/2) [(\lambda^2 - 1)(1 - \mu^2)]^{1/2} \cos \phi, \quad (29)$$

$$y = (R/2) [(\lambda^2 - 1)(1 - \mu^2)]^{1/2} \sin \phi, \quad (30)$$

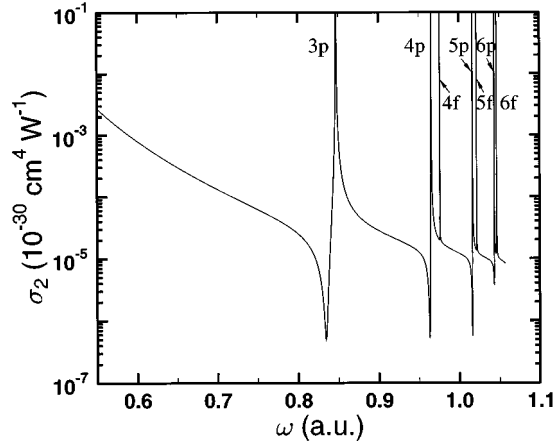


FIG. 1. Generalized cross section, in the weak-field limit, for two-photon ionization of  $\text{H}_2^+$  (at the equilibrium internuclear separation 2 a.u.) by linearly polarized light of angular frequency  $\omega$ . The internuclear axis is oriented along the polarization axis.

$$z = (R/2)\lambda\mu, \quad (31)$$

and writing  $\nabla = (\partial/\partial x, \partial/\partial y, \partial/\partial z)$  we have

$$\frac{\partial}{\partial x} = \frac{2}{R} \sqrt{(\lambda^2 - 1)(1 - \mu^2)} \left[ \frac{\cos\phi}{(\lambda^2 - \mu^2)} \left( \lambda \frac{\partial}{\partial \lambda} - \mu \frac{\partial}{\partial \mu} \right) - \frac{\sin\phi}{(\lambda^2 - 1)(1 - \mu^2)} \frac{\partial}{\partial \phi} \right], \quad (32)$$

$$\frac{\partial}{\partial y} = \frac{2}{R} \sqrt{(\lambda^2 - 1)(1 - \mu^2)} \left[ \frac{\sin\phi}{(\lambda^2 - \mu^2)} \left( \lambda \frac{\partial}{\partial \lambda} - \mu \frac{\partial}{\partial \mu} \right) + \frac{\cos\phi}{(\lambda^2 - 1)(1 - \mu^2)} \frac{\partial}{\partial \phi} \right], \quad (33)$$

$$\frac{\partial}{\partial z} = \frac{2}{R} \frac{1}{(\lambda^2 - \mu^2)} \left( (\lambda^2 - 1)\mu \frac{\partial}{\partial \lambda} + (1 - \mu^2)\lambda \frac{\partial}{\partial \mu} \right). \quad (34)$$

As mentioned above, we consider the molecule to be oriented along the polarization axis of the laser field, and since we ignore the motion of the nuclei, the projection of the electronic angular momentum along the internuclear axis (the  $z$  axis) is conserved. Therefore we need consider only transitions to  $\Sigma$  states, i.e.,  $m=0$ , and the electron wave function is independent of  $\phi$ . Plummer and McCann used a Slater-type basis for the electron wave function. We use an orthogonal basis:

$$u_\nu(\lambda) = \sqrt{-2i\kappa R} e^{i\kappa R(\lambda-1)} L_\nu[-2i\kappa R(\lambda-1)], \quad (35)$$

$$v_\eta(\mu) = P_\eta(\mu), \quad (36)$$

where  $L_\nu(x)$  and  $P_\eta(\mu)$  are Laguerre and Legendre polynomials, respectively, with  $\nu$  and  $\eta$  non-negative integers, and where  $\kappa$  lies in the upper right quadrant of the complex plane so that the functions  $u_\nu(\lambda)$  can represent both closed (bound) and open (outgoing-wave) channels. The matrix representations of  $V_\pm$ , denoted as  $\underline{V}_\pm$ , can be expressed as sums of

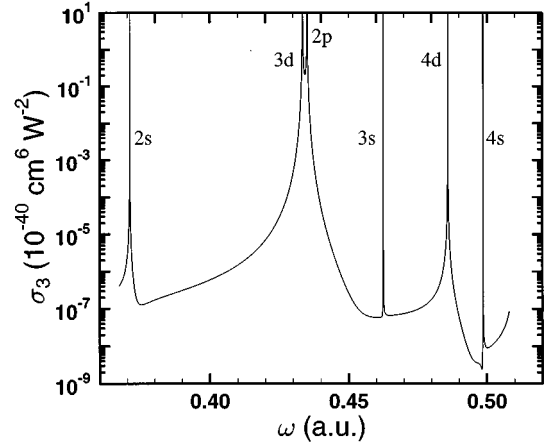


FIG. 2. Same as Fig. 1 but for three-photon ionization.

direct products of smaller matrices, which are sparse and at most quintidiagonal. All matrix elements of  $\underline{H}$ ,  $\underline{S}$ , and  $\underline{V}_\pm$  can be evaluated in closed form. Furthermore,  $\underline{s}_\lambda$  and  $\underline{s}^\mu$  are unit matrices, and  $\underline{s}_\lambda$ ,  $\underline{s}^\mu$ ,  $\underline{h}_\lambda$ , and  $\underline{h}^\mu$  are also sparse and at most quintidiagonal.

We denote the ac quasienergy of the electron as  $E_{ac}$ , which we can express as  $E_{ac} = E_0 + \Delta - i\Gamma/2$ , where  $E_0$  is the unperturbed initial (ground-state) energy and where  $\Delta$  and  $\Gamma$  are the induced shift and width, respectively. The Rayleigh-Schrödinger perturbation series is (see, e.g., [5])

$$E_{ac} = \sum_{n=0}^{\infty} E^{(2n)} F^{2n}, \quad (37)$$

where  $E^{(0)} = E_0$  and where  $\text{Im}E^{(2n)} = 0$  for  $n < N_0$ , with  $N_0$  the minimum number of photons that the molecule must absorb to ionize. In lowest nonvanishing order the rate for ionization is

$$\Gamma_{N_0} \equiv -2F^{2N_0} \text{Im}E^{(2N_0)} \quad (38)$$

$$= -2 \text{Im} \langle \phi_0 | V_- G(E_0 + \omega) \cdots V_- G(E_0 + N_0\omega + i\epsilon) \times V_+ \cdots G(E_0 + \omega) V_+ | \phi_0 \rangle, \quad (39)$$

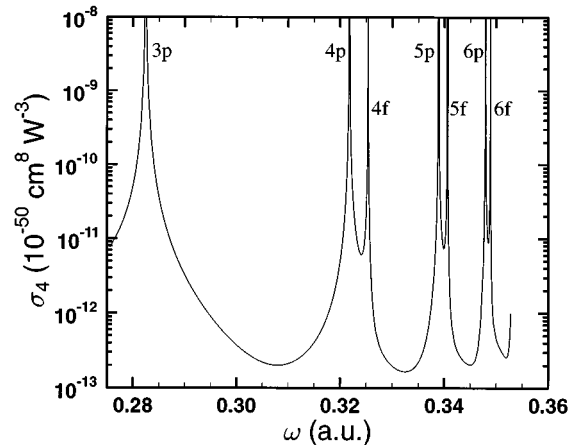


FIG. 3. Same as Fig. 1 but for four-photon ionization.

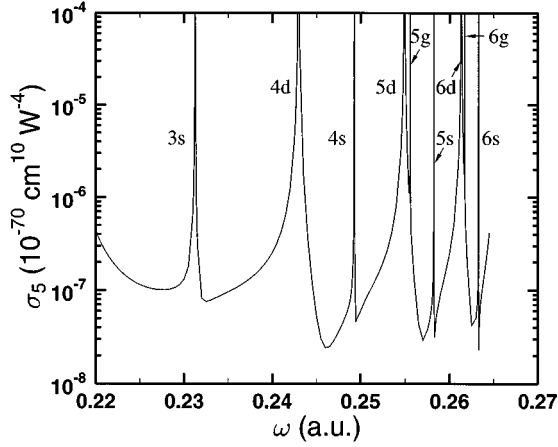


FIG. 4. Same as Fig. 1 but for five-photon ionization.

where the ket  $|\phi_0\rangle$  represents the initial unperturbed electronic state, and where  $\epsilon$  is positive but infinitesimal. In the weak-field limit the generalized ionization cross section is

$$\sigma_{N_0} = \omega \Gamma_{N_0} / I^{N_0}, \quad (40)$$

where  $I \equiv cF^2 / (8\pi)$  is the intensity of the light.

### III. RESULTS

In Figs. 1–5 we show the cross section  $\sigma_{N_0}$  for weak-field ionization of  $\text{H}_2^+$  at the equilibrium internuclear separation of 2 a.u. versus the frequency  $\omega$  of the linearly polarized light, where  $N_0$  (the minimum number of photons that must be absorbed for ionization to occur) varies from 2 to 6. The results in Figs. 1 and 2 agree with the cross sections for two- and three-photon ionization calculated at weak fields by Plummer and McCann [1]. There is a lot of resonance structure, and by studying the electronic potential energy curves from  $R=0$  to  $R=2$  a.u. we can identify the intermediate states involved in the resonances; we have labeled them using united-atom-limit quantum numbers. Most of the reso-

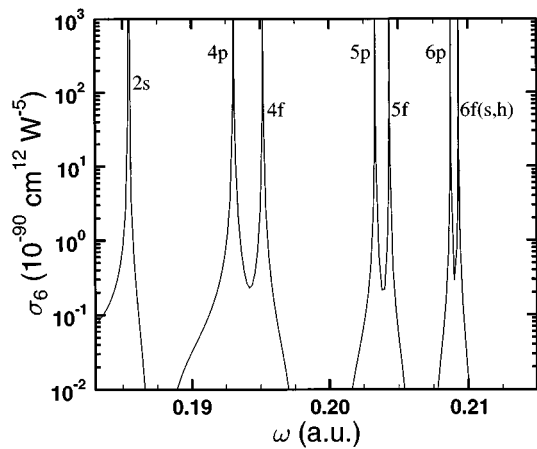


FIG. 5. Same as Fig. 1 but for six-photon ionization. The  $6s$  and  $6h$  resonances occur at almost the same frequency as the  $6f$  resonance, but they are much narrower than the latter.

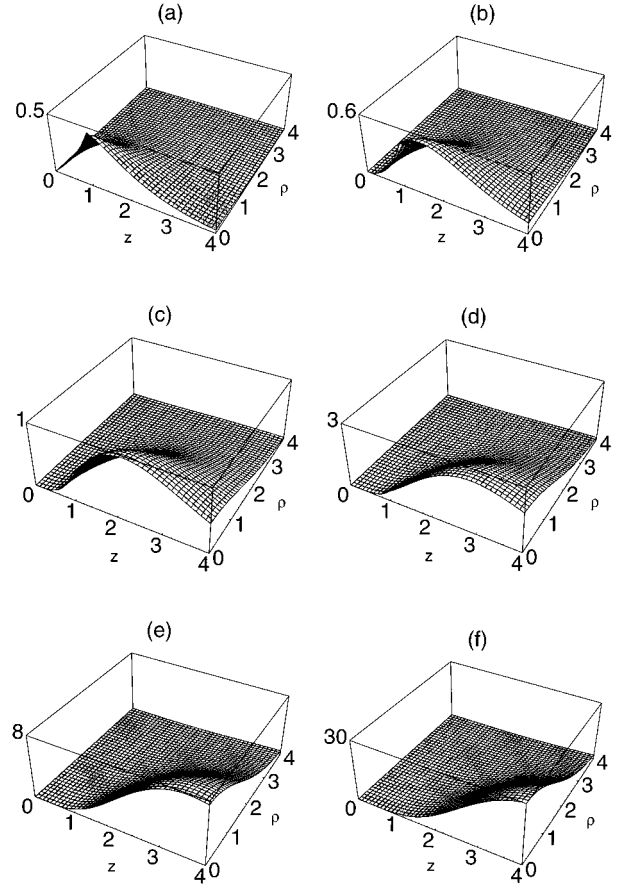


FIG. 6. Plots of  $z^M \sqrt{P_{1s}(\rho, z)}$  in cylindrical coordinates where  $P_{1s}(\rho, z)$  is the ground-state electron probability distribution of  $\text{H}_2^+$  at an internuclear separation of 2 a.u. with  $P_{1s}(\rho, z)$  normalized so that  $2\pi \int \rho d\rho dz P_{1s}(\rho, z) = 1$ . The horizontal plane is the  $\rho z$  plane, the positive  $z$  axis points towards the reader and is along the internuclear axis, and the  $\rho$  axis points away from the reader. (a)  $M=1$ , (b)  $M=2$ , (c)  $M=3$ , (d)  $M=4$ , (e)  $M=5$ , and (f)  $M=6$ .

nances arise from  $(N_0 - 1)$ -photon excitations to electronic states, but the  $2p$  resonance in Fig. 2 arises from a one-photon transition, and the  $2s$  resonance in Fig. 5 arises from a four-photon transition—both of these transitions are  $(N_0 - 2)$ -photon excitations. Some of the resonances are very narrow in the sense that they influence the cross section only at very small detunings from exact resonance, while other resonances are broad in the sense that they are prominent at quite large detunings. (We cannot speak of a full width at half maximum since in the weak-field limit the resonance peaks are infinitely high.) For example, in Fig. 1 (two-photon ionization) we see that the  $p$  resonances are relatively broad while the  $f$  resonances are narrow, in Fig. 2 (three-photon ionization) the  $d$  resonances are relatively broad while the  $s$  resonances are narrow, in Fig. 3 (four-photon ionization) the  $p$  resonances are relatively broad while the  $f$  resonances are narrow, in Fig. 4 (five-photon ionization) the  $d$  resonances are broader than the  $s$  resonances, and in Fig. 5 (six-photon ionization) the  $f$  resonances are about as prominent as the  $p$  resonances. We can understand these features, to some extent, if we adopt rather crude approximations to the Green's functions  $G(E_0 + L\omega)$  for  $L \neq N_0$ . Thus if the intermediate resonant state has energy  $E_{\text{res}}$  and is rep-

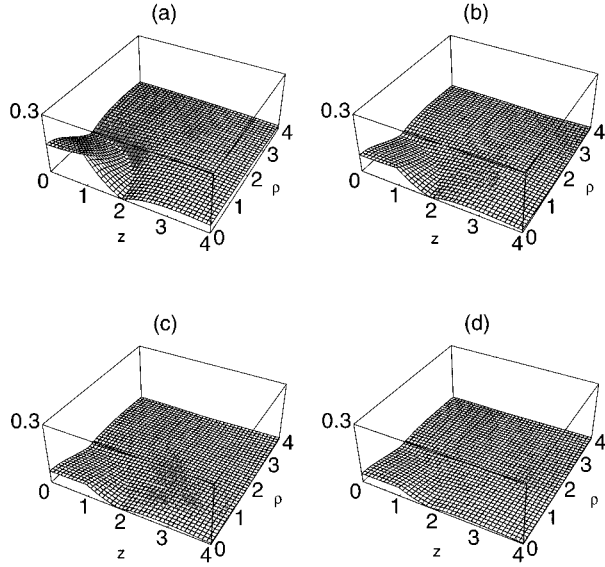


FIG. 7. Plots of  $\sqrt{P_{\text{res}}(\rho, z)}$  in cylindrical coordinates where  $P_{\text{res}}(\rho, z)$  is the electron probability distribution in an intermediate resonant  $s$  state, normalized so that  $2\pi \int d\rho dz P_{\text{res}}(\rho, z) = 1$ . (a)  $2s$ , (b)  $3s$ , (c)  $4s$ , and (d)  $5s$ .

resented by  $|\phi_{\text{res}}\rangle$ , and if the resonance is excited by  $M$  photons, we write

$$G(E_0 + M\omega) \approx \frac{|\phi_{\text{res}}\rangle\langle\phi_{\text{res}}|}{E_0 + M\omega - E_{\text{res}}}, \quad (41)$$

while for  $L \neq M, N_0$  we follow Gold and Bebb [6], and make the closure approximation

$$G(E_0 + L\omega) \approx \frac{1}{E_0 + L\omega - E_{\text{av}}}, \quad (42)$$

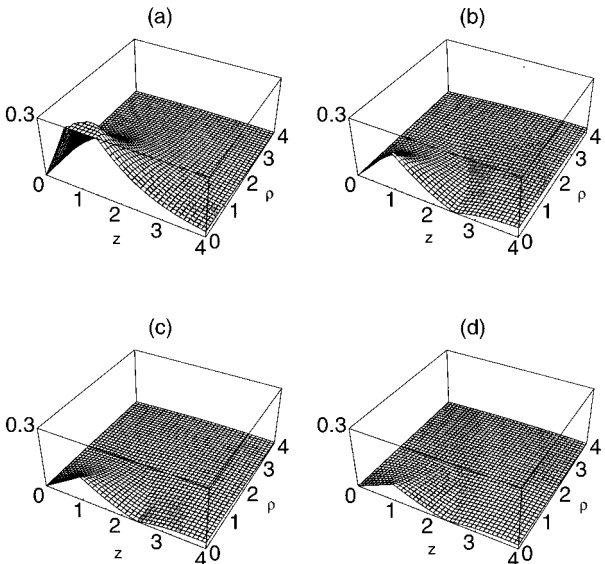


FIG. 8. Same as Fig. 7 but for an intermediate resonant  $p$  state. (a)  $2p$ , (b)  $3p$ , (c)  $4p$ , and (d)  $5p$ .

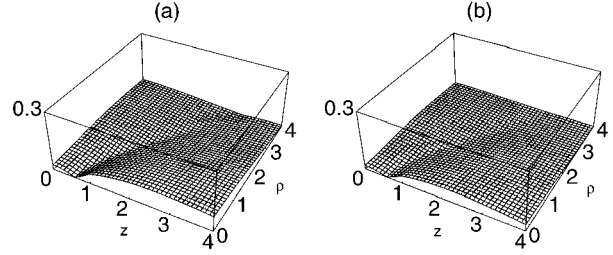


FIG. 9. Same as Fig. 7 but for an intermediate resonant  $d$  state. (a)  $3d$  and (b)  $4d$ .

where  $E_{\text{av}}$  is some average energy. We also note that

$$\text{Im}G(E_0 + N_0\omega + i\epsilon) = -\pi\delta(E_0 + N_0\omega - H) \quad (43)$$

$$= -\pi k \int d^2\hat{\mathbf{k}} |\phi_{\mathbf{k}}\rangle\langle\phi_{\mathbf{k}}|, \quad (44)$$

where  $|\phi_{\mathbf{k}}\rangle$  is a continuum eigenvector of  $H$  (normalized on the momentum scale) with energy eigenvalue  $k^2/2 = E_0 + N_0\omega$ . Using Eqs. (39), (41), (42), and (44) we have, for  $E_0 + M\omega \approx E_{\text{res}}$ ,

$$\Gamma_{N_0} \approx \frac{2\pi k |\langle\phi_{\text{res}}|V^M|\phi_0\rangle|^2}{(E_0 + M\omega - E_{\text{res}})^2} \prod_{L=1, L \neq M}^{N_0-1} \left( \frac{1}{E_0 + L\omega - E_{\text{av}}} \right)^2 \times \int d^2\hat{\mathbf{k}} |\langle\phi_{\mathbf{k}}|V^{N_0-M}|\phi_{\text{res}}\rangle|^2. \quad (45)$$

For a fixed but small detuning from resonance, the relative prominence of a particular resonance depends primarily on the factor  $|\langle\phi_{\text{res}}|V^M|\phi_0\rangle|^2$ , which measures the strength of excitation from the initial state to the resonant state [7]. Within the length gauge, this factor depends strongly on the degree of overlap of  $z^M\langle\mathbf{x}|\phi_0\rangle$  and  $\langle\mathbf{x}|\phi_{\text{res}}\rangle$ . In Fig. 6 we show three-dimensional plots of  $z^M\sqrt{P_{1s}(\rho, z)}$  for  $M=1-6$  and  $z>0$ , where  $P_{1s}(\rho, z) = |\langle\mathbf{x}|\phi_0\rangle|^2$  and  $\rho = \sqrt{x^2 + y^2}$ . In Figs. 7–10 we show three-dimensional plots of  $\sqrt{P_{\text{res}}(\rho, z)}$ , where  $P_{\text{res}}(\rho, z) = |\langle\mathbf{x}|\phi_{\text{res}}\rangle|^2$ , for  $s, p, d$ , and  $f$  resonances, respectively. Inspection of these figures reveals that a relatively large overlap of  $z^M\sqrt{P_{1s}(\rho, z)}$  with  $\sqrt{P_{\text{res}}(\rho, z)}$  corresponds to a relatively prominent resonance.

Up to now we have only shown results for ionization rates in lowest nonvanishing order of perturbation theory. We have calculated the coefficients  $E^{(2n)}$  to higher order,

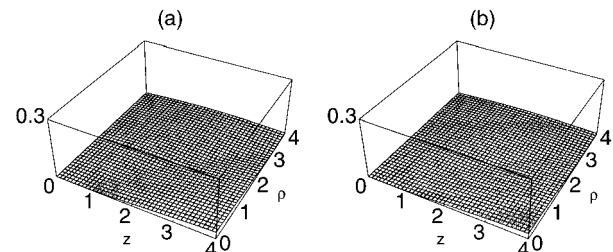


FIG. 10. Same as Fig. 7 but for an intermediate resonant  $f$  state. (a)  $4f$  and (b)  $5f$ .

TABLE I. Rates, in  $s^{-1}$ , for ionization of  $H_2^+$  at an internuclear separation of 2 a.u. and at a wavelength of 228 nm. Some of the results at lower intensities reported on in Ref. [3] were recently revised (private communication with K. Kulander) and we give the revised numbers here.

$I$ (W/cm <sup>2</sup> )	Ionization rate ( $s^{-1}$ )		
	Ref. [3]	Ref. [2]	Present
$5 \times 10^{13}$	$6 \times 10^7$		$1.3 \times 10^8$
$1 \times 10^{14}$	$3 \times 10^{10}$		$2.1 \times 10^{11}$
$2 \times 10^{14}$	$4 \times 10^{11}$		$1.0 \times 10^{12}$
$3 \times 10^{14}$	$4 \times 10^{12}$	$3 \times 10^{12}$	$5.7 \times 10^{12}$
$3.9 \times 10^{14}$	$2 \times 10^{13}$	$1 \times 10^{13}$	$1.6 \times 10^{13}$
$5 \times 10^{14}$	$3 \times 10^{13}$	$5 \times 10^{13}$	$4.5 \times 10^{13}$
$6 \times 10^{14}$		$2 \times 10^{13}$	$9.5 \times 10^{13}$

$n > N_0$ , but the perturbation series does not converge in the immediate vicinity of a resonance [8]. However, Chelkowski *et al.* [2] and Mies *et al.* [3] have calculated ionization rates at the wavelength 228 nm, i.e.,  $\omega = 0.2$  a.u., for various intensities of the laser light. At low intensities, and at the frequency  $\omega = 0.2$  a.u., the molecule must absorb at least six photons to ionize. This frequency is quite far from any resonance, as is evident from Fig. 5, and hence the perturbation series converges for moderately weak values of the intensity  $I$ , but as  $I$  increases the electronic energy levels shift, and various levels move in and out of resonance; applying the ratio test, we find that the radius of convergence of the perturbation series is the intensity  $7.6 \times 10^{13}$  W/cm<sup>2</sup>. Nevertheless, we can resum the perturbation series using the Padé method [9], and, except at intensities in the immediate vicinity of a resonance, we obtain a finite (converged) value for the ac quasienergy for the *adiabatic* level that originates from the electronic ground state. In Table I we compare our estimates of the rate for ionization from this level (the internuclear separation is again 2 a.u.) with those of Chelkowski *et al.* and Mies *et al.* At the highest intensity considered,  $6 \times 10^{14}$  W/cm<sup>2</sup>, the shift of the ground-state level relative to the continuum is 0.135 a.u., and six photons are still sufficient to ionize the molecule, but at a moderately higher intensity,  $8.8 \times 10^{14}$  W/cm<sup>2</sup>, the shift relative to the continuum is 0.2 a.u., and the minimum number of photons which the molecule must absorb to ionize is seven.

#### IV. REMARKS

The separability of the electronic Hamiltonian in prolate spheroidal coordinates, in conjunction with our chosen basis, allowed us to calculate many terms of the Rayleigh-Schrödinger perturbation series with considerable efficiency and accuracy over a fairly wide frequency range. However, for small or large values of the frequency  $\omega$  these terms are more difficult to calculate—convergence with respect to increasing basis size is hard to achieve. For example, we were unable to calculate to satisfactory accuracy seven-photon ionization in lowest nonvanishing order of perturbation theory. To what can we attribute this limitation? We are not sure of the answer, but it may be useful to note the following. Photoabsorption is most likely to take place near one or other of the nuclei, particularly at high frequencies. Each time a photon is absorbed near one of the nuclei, say nucleus

$b$ , the electronic angular momentum about that nucleus changes by unity. However, our basis, as defined by Eqs. (35) and (36), cannot easily represent the centrifugal barrier repulsion about this nucleus, i.e., the basis cannot easily describe the functional form  $r_b^l$  for  $r_b \approx 0$  since  $\lambda \rightarrow 1$  and  $\mu \rightarrow 1$  as  $r_b \rightarrow 0$ . Recognizing that  $\mu - 1 \propto r_b$  when  $r_b \approx 0$  and that  $\mu + 1 \propto r_a$  when  $r_a \approx 0$ , one might think it expedient to replace the basis functions  $P_\eta(\mu)$  by functions  $v'_\eta(\mu)$  where  $v'_\eta(\mu) = \cosh(\kappa' R \mu)(1 - \mu^2)^\eta$ , in the case of even parity, or  $v'_\eta(\mu) = \sinh(\kappa' R \mu)(1 - \mu^2)^\eta$  in the case of odd parity. Unfortunately, the functions  $v'_\eta(\mu)$  are not orthogonal and are nearly linearly dependent, as can be seen from Table II where we show the ten eigenvalues of the  $10 \times 10$  overlap matrix whose elements are

$$t^{\eta' \cdot \eta} = a_{\eta'} a_\eta \int_{-1}^1 d\mu v'_{\eta'}(\mu) v'_\eta(\mu), \quad (46)$$

in the case of even parity basis functions with  $\kappa' = 0.15$ , where  $0 \leq \eta', \eta \leq 9$ , and where  $a_\eta^2 = 1 / \int_{-1}^1 d\mu v_\eta'^2(\mu)$ . Many of the eigenvalues are extremely small compared to unity, indicating the onset of linear dependence.

In summary, we have outlined a method for calculating terms of the Rayleigh-Schrödinger perturbation series for multiphoton ionization of  $H_2^+$ , at a fixed internuclear separation, and we have presented results of an application. The method is highly efficient provided that  $\omega$  is neither too small nor too high; but for small or large values of  $\omega$ , our basis, and perhaps even the prolate spheroidal coordinate system, is unsuitable for treating multiphoton ionization of  $H_2^+$ . Since we have frozen the positions of the nuclei we have not incorporated dissociation. We note, however, that Chelkowski *et al.* [10] recently solved the time-dependent

TABLE II. Eigenvalues of the overlap matrix whose elements are  $t^{\eta' \cdot \eta}$  (see text).

$2.3 \times 10^{-14}$	$3.9 \times 10^{-5}$
$5.0 \times 10^{-12}$	$8.6 \times 10^{-4}$
$5.0 \times 10^{-10}$	$1.5 \times 10^{-2}$
$3.1 \times 10^{-8}$	$2.0 \times 10^{-1}$
$1.3 \times 10^{-6}$	$3.1 \times 10^0$

Schrödinger equation for  $H_2^+$  in a strong laser field, including the motion of the nuclei; they found that at larger inter-nuclear separations there is a strong interplay between dissociation and ionization.

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