Static field tunneling ionization of H$_2^+$

R. Barnett[1] and G. N. Gibson[2]

[1]*Department of Physics, The Ohio State University, Columbus, Ohio 43210*
[2]*Physics Department, University of Connecticut, Storrs, Connecticut 06269*

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We present tunneling ionization rates from a double-well potential in the presence of an external dc electric field in order to better understand the behavior of molecules in strong laser fields. Our calculations confirm the well-established peak in the ionization rate as a function of internuclear separation at a critical separation R_{max}. However, we also find that R_{max} is a function of the external field strength F such that $R_{max}(F)F$ is approximately constant. Because these numerical calculations make no assumptions beyond the shape of the potential well, we can test commonly used approximations to the shift in the energy levels as a function of internuclear separation and field strength. Finally, we find that the tunneling ionization rate is not a monotonic function of the field strength showing a pronounced minimum and thus is qualitatively different from tunneling ionization rates in atoms. To our knowledge, this behavior has not been predicted previously for molecules in strong fields. [S1050-2947(99)07606-4]

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Experiments that study the behavior of atoms and molecules in strong laser fields have been taking place for nearly two decades. To interpret some of the data obtained, the demand for ionization models has been high. Fortunately, several models have been developed that predict the ionization rates or threshold intensities for ionization of atoms in intense laser fields. Among the techniques used for these models are classical barrier suppression ionization (BSI) [1], quasistatic tunneling [2], and the full time-dependent treatment of the Schrödinger equation (TDSE) [3]. These techniques have been sufficient for interpreting most atomic data [3].

The study of molecules is more complex due to the extra degrees of freedom. On the one hand, even the simplest model of BSI leads to different and interesting behavior [4]. However, BSI makes many assumptions and it does not predict ionization rates. On the other hand, when applied to molecules, the TDSE is very time consuming and one cannot always interpret the physical mechanism behind some of its various results [5]. It is also difficult to apply the TDSE to complex molecules. The interpretation of molecular data has been impeded by the simplicity of the first model and the complexity of the second.

Only recently has a rigorous yet practical tunneling ionization model for arbitrary potentials been developed [6]. This general tunneling model uses a nonperturbative technique for computing tunneling ionization rates from arbitrary one-dimensional (1D) potential wells. In particular, the problem of determining the ionization rates and Stark shifts of 1D wells can be reduced to calculating the spectral density $\rho(E)$ as a function of energy E using the Weyl-Titchmarsh-Kodaira spectral theorem [7]. Although the limitation to 1D wells might seem overly restrictive, this method is well suited to strong field ionization because the ionization occurs, for the most part, in the direction of the applied electric field, essentially reducing this to a 1D problem. $\rho(E)$ consists of Lorentzian-like resonances whose center positions reflect the Stark shift of the energy levels and widths give the decay rates. In this paper we will discuss the application of this model to H$_2^+$, the simplest of molecules.

The most striking feature of previous work on H$_2^+$ in intense fields is the strong dependence of the ionization rate on internuclear separation due to electron localization [5,8]. This effect is also manifest in BSI through a minimum in the appearance intensity at a critical separation [4]. Our tunneling calculations also exhibit this nonmonotonic behavior of the ionization rate of H$_2^+$ as a function of internuclear separation, featuring a single peak at R_{max}. However, our calculations also show that the value of R_{max} depends on dc field strength. While the nonmonotonic behavior is predicted by both BSI and the TDSE, since the BSI does not give rates, it is unable to predict the shift in R_{max}. Moreover, published results from TDSE calculations also do not appear to show this effect. In addition, results from the TDSE have a double peak in the ionization rate [5], which we do not see. We next found that results from perturbation theory for the shift of the energy level as a function of internuclear separation and dc field strength agree well with our calculations for small fields and large internuclear separations. Our final result, to our knowledge, has not been predicted before: We observed that the ionization rate of H$_2^+$ as a function of dc field strength is nonmonotonic. This is surprising because perturbation theory always yields ionization rates as a function of field strength that are monotonic. Also, atomic tunneling rates are known to be monotonic as a function of field strength. The only other situation known to give nonmonotonic rates is very high field stabilization [9].

Throughout our calculations, we used the soft Coulomb potential [10]

$$V(X) = \frac{1}{\sqrt{(x+R/2)^2+a^2}} + \frac{1}{\sqrt{(x-R/2)^2+a^2}} - Fx, \quad (1)$$

where R is the internuclear separation, $a=\sqrt{2}$, and F is the dc field strength. This choice for a gives the binding energy of a single well equal to 0.5 a.u. For a given R and F, $V(x)$
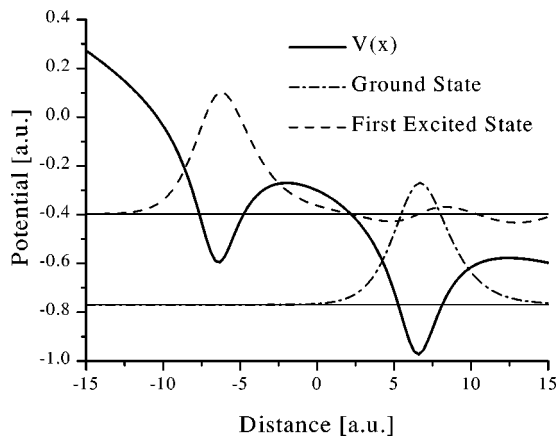
FIG. 1. Wave functions for the ground and first excited states of a double-well potential plotted at their respective energy levels. All quantities are given in atomic units.

was used to calculate the spectral density as a function of energy E. The widths of the peaks of $\rho(E)$ give the respective ionization rates [6].

Figure 1 shows the ground-state and first-excited-state wave functions ψ_0 and ψ_1 superimposed over $V(x)$ for a fixed value of R and F. Although the ground and first excited states of a symmetric double-well potential correspond to the symmetric and antisymmetric wave functions, a very small external field is sufficient to break the symmetry. The ground and first excited states quickly evolve into wave functions localized in the down-field and up-field wells, respectively. The ionization rate of the ground state is much smaller than the excited state. The excited state also shows the most interesting behavior and is easily populated by trapping the electron in the up-field well. Because of the implications of this behavior, we focused on ionization from the first excited state of H_2^+ in our calculations.

Figure 2 shows our data for the energy of the excited state as a function of internuclear separation and dc field strength compared with the Stark shifted energies approximated by perturbation theory:

$$E_1 = E_{atom} - \frac{1}{\sqrt{R^2 + a^2}} + \frac{FR}{2}, \qquad (2)$$

where E_{atom} is the binding energy of an individual well. Notice that the results agree reasonably well for small F and large R. This confirms the validity of commonly used approximations for the energy levels of molecules in strong laser fields [4,11].

Figure 3 shows ionization rates as a function of R for different field strengths. The first aspect of these plots that we will consider is their nonmonotonic behavior: Each of these graphs increases to a peak value at around 8 a.u. (R_{max}) and then decreases monotonically. The explanation for this behavior is obtained by considering the potential $V(x)$ in Fig. 4. When R is small, the respective potential well resembles that of helium. For ionization to occur, the electron must tunnel through the relatively large outer barrier seen in Fig. 4(a) making the respective ionization rate small. As R increases, the effective size of this outer barrier decreases while the effective size of the central barrier in-
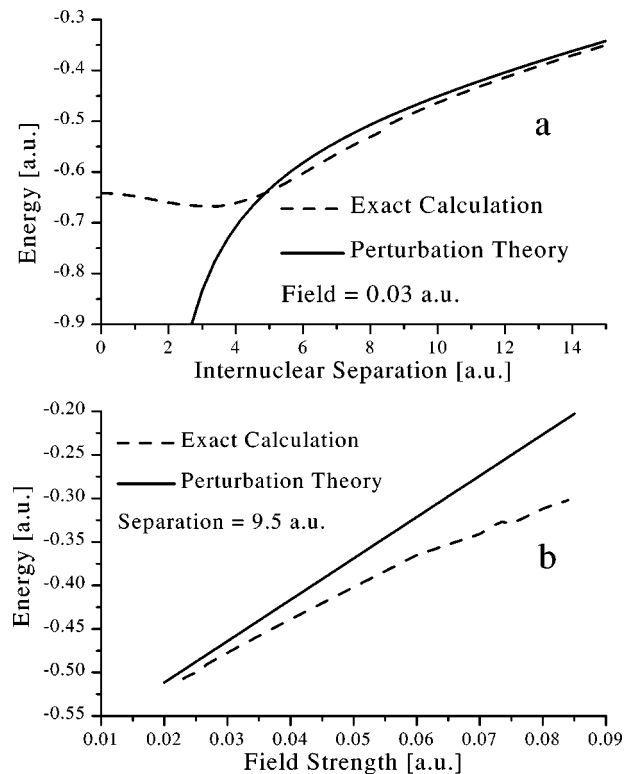

FIG. 2. Energy of the first excited state as a function of internuclear separation and dc field strength.

creases for the up-field well. The potential for $R = R_{max}$ is shown in Fig. 4(b). For this case, an electron merely needs to tunnel through the central barrier for ionization to occur. Since the size of this central barrier is small, the ionization rates for R close to R_{max} are at a maximum. Finally, as R continues to increase, the previously small central barrier becomes larger. It follows that the ionization rates will decrease to the case of a hydrogen atom as the internuclear separation approaches infinity. The implication of this is seen in our results (Fig. 3). Very similar results have also been found experimentally by Gibson et al. [8]. Using short-pulsed lasers and time-of-flight spectroscopy, the ionization rate of H_2^+ under intense laser fields was seen to peak at a value similar to our R_{max}.

This dependence of the ionization rate on internuclear separation has been seen by Zuo and Bandrauk using the
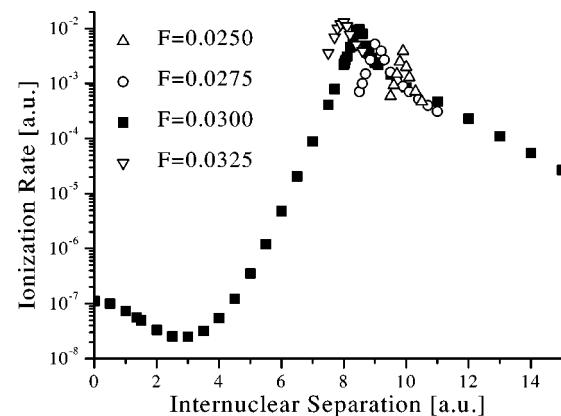

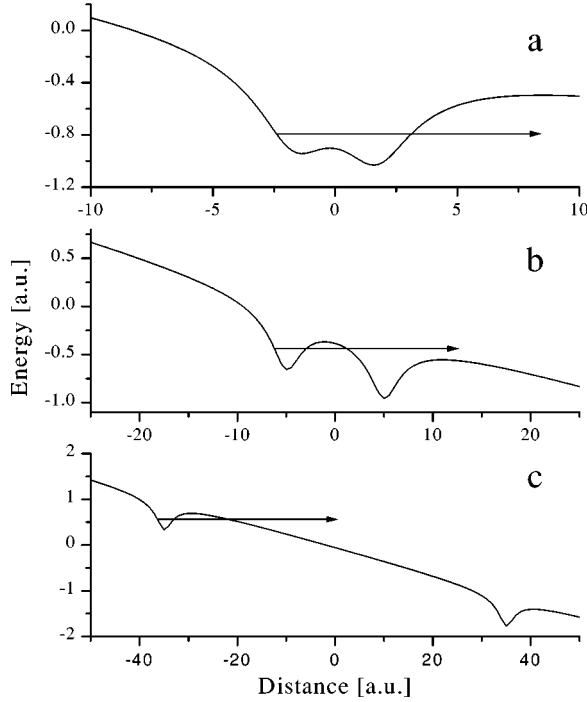FIG. 3. Ionization rate as a function of internuclear separation for fixed dc field strength.

FIG. 4. Double-well potential for three different internuclear separations.

FIG. 5. Ionization rate as a function of dc field strength for fixed internuclear separation and the corresponding time-averaged rate.

TDSE [5] and generally agrees with our value of R_{max}. However, the exact shape of the curve is somewhat different. For some laser field intensities, a double peak in the ionization rate as a function of internuclear separation was exhibited with a maximum occurring at approximately 7 and 9 a.u. in the TDSE calculations. The two peaks were associated with two different effects. One peak is related to the effect described above, while the other peak appears to be the result of a true time-dependent quantum-mechanical effect. Our quasistatic tunneling calculations tend to support this interpretation as we would not see any time-dependent effects.

The most interesting aspect of Fig. 3 is the dependence of R_{max} on F. So far, we have not found a simple explanation for this. Because BSI does not give ionization rates, but only appearance intensities, it could not predict such an effect. Furthermore, this behavior apparently has not been seen in TDSE calculations. While the reason for this shift is unclear, we have found that the product FR_{max} is approximately constant.

Finally, we will discuss the nonmonotonic behavior of the ionization rate as a function dc field strength $\Gamma(F)$. To our knowledge, this phenomenon has never been seen before. Our investigation was initially motivated by the manner in which the curves in Fig. 3 cross. For instance, one sees that for some internuclear separations, the curve with the largest field strength does not always have the highest ionization rate. Figure 5 shows the ionization rate as a function of field strength for a fixed internuclear separation. The ionization rate initially rises much faster than atomic tunneling rates and then drops sharply before approaching a more tunneling-like dependence. No further modulations in the rate were seen at larger field strengths. Calculations for different values of R gave the same general shape, although the local
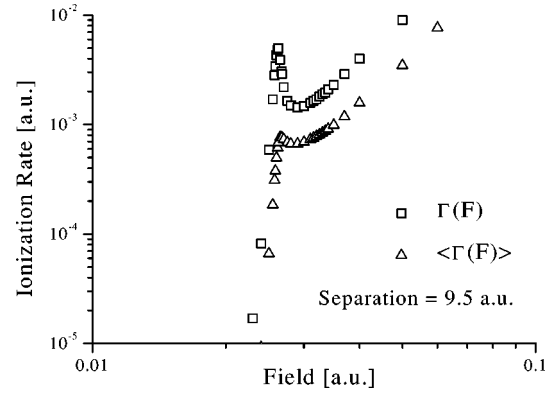
maximum and minimum in the rate occurred at different field strengths. The values of R and F at the peaks in $\Gamma(F)$ correspond to the peaks in Fig. 3. As far as we know, this nonmonotonic behavior is not seen in TDSE calculations.

Finding such behavior leads one to consider methods of observing the nonmonotonic behavior of $\Gamma(F)$ experimentally. First, it needs to be realized that dc fields as strong as those used in our calculations have never been produced. However, the ac fields produced by high-intensity laser systems do have peak intensities comparable to the values of F used in our calculations. With this motivation, we took the time average of $\Gamma(F)$ to find the quasistatic ac rate [2] given by

$$\langle \Gamma(F) \rangle = \frac{2}{T} \int_0^{T/2} \Gamma\left[F \cos\left(\frac{2\pi}{T}\right) t \right] dt. \qquad (3)$$
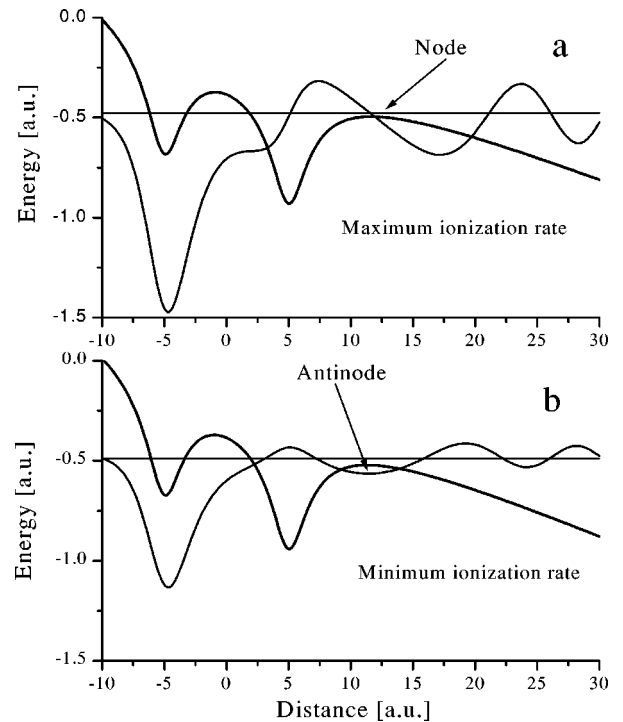

FIG. 6. Wave functions at the local (a) maximum and (b) minimum ionization rates.

We found that the nonmonotonic behavior of $\Gamma(F)$ did indeed survive the time average, as seen in Fig. 5.

In trying to account for this anomalous nonmonotonic behavior, we looked at the potential for H_2^+ and the respective wave functions. Figure 6 shows the cases for the local maximum and local minimum of $\Gamma(F)$. The ionization rate in Fig. 6(b) is less than in Fig. 6(a) even though the field strength is higher and the wave function is less bound. However, one sees that for the maximum ionization rate there is a node at the potential barrier and for the minimum ionization rate there is an antinode at the potential barrier. This was found to be the case for three different internuclear separations. Thus the ionization behavior appears to be connected with the shape of the wave function, which may result from an interference effect between the two barriers.

In conclusion, we have applied a recently developed tunneling ionization model to the molecule H_2^+. Our results agree well with Stark shift approximations for large internuclear separations and small dc field strengths. We calculated $\Gamma(R)$, which peaked at values similar to those formerly calculated from the TDSE and BSI. We also saw that R_{max} shifts for different field strengths. To our knowledge, this has never been seen before. The ways in which the curves in Fig. 3 cross suggested the nonmonotonic dependence of ionization rate on field strength. This remarkable behavior is displayed in Fig. 5 and may be observable experimentally.

[1] S. Augst, D. Strickland, D. D. Meyerhofer, S. L. Chin, and J. H. Eberly, Phys. Rev. Lett. **63**, 2212 (1989).

[2] M. V. Ammosov, N. B. Delone, and V. P. Krainov, Zh. Éksp. Teor. Fiz. **91**, 2008 (1986) [Sov. Phys. JETP **64**, 1191 (1986)].

[3] J. L. Krause, K. L. Schafer, and K. C. Kulander, Phys. Rev. A **45**, 4998 (1992); B. Walker, B. Sheehy, L. F. DiMauro, P. Agostini, K. J. Schafer, and K. C. Kulander, Phys. Rev. Lett. **73**, 1227 (1994).

[4] J. H. Posthumus, A. J. Giles, M. R. Thompson, and K. Codling, J. Phys. B **29**, 5811 (1996).

[5] T. Zuo and A. D. Bandrauk, Phys. Rev. A **52**, R2511 (1995).

[6] G. N. Gibson, G. Dunne, and K. J. Bergquist, Phys. Rev. Lett. **81**, 2663 (1998).

[7] *Eigenfunction Expansions Associated with Second-Order Differential Equations, Vols. I and II*, edited by E. C. Titchmarsh (Oxford University Press, Oxford, 1946); K. Kodaira, Am. J. Math. **71**, 921 (1949).

[8] G. N. Gibson, M. Li, C. Guo, and J. Neira, Phys. Rev. Lett. **79**, 2022 (1997).

[9] M. Pont and M. Gavrila, Phys. Rev. Lett. **65**, 2362 (1990); R. J. Vos and M. Gavrila, *ibid.* **68**, 170 (1992).

[10] J. Javanainen, J. H. Eberly, and Q. Su, Phys. Rev. A **38**, 3430 (1988).

[11] P. Dietrich, D. T. Strickland, and P. B. Corkum, J. Phys. B **26**, 2323 (1993).