Enhanced ionization of molecular hydrogen in very strong fields

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(Received 7 September 1999; published 12 April 2000)

On the basis of a nonperturbative *ab initio* calculation for a hydrogen molecule in an electric field within a fully correlated, three-dimensional description, it is found that the ionization rate exhibits a pronounced enhancement at a specific internuclear distance. A general quantum-mechanical explanation for this enhancement is presented that is based on (diabatic) curve crossings and should be applicable to most diatomic molecules.

A molecule will often undergo Coulomb explosion, if it is exposed to a sufficiently strong laser pulse, since the laser field will induce (multiple) ionization that finally leads to a breakup of the system due to the internuclear repulsion that is no longer compensated by the electrons. A striking feature observed in such experiments is a sharp kinetic-energy distribution of the ionic fragments (see, e.g., [1] and references therein). Assuming vertical transitions to the repulsive potential curve on which the Coulomb explosion takes place, the observed narrow energy distribution indicates that ionization occurs within a small range of internuclear distances. Otherwise, a broad energy distribution should be found due to the steepness of the repulsive potential curve.

A possible reason for this observation could be that the ionization rate is strongly enhanced at certain values of the internuclear distance. The origin of such an enhancement (if existent) is evidently of paramount interest, since it is a truly molecular strong-field process. An explanation for enhanced ionization in the case of molecular ions was given in rather general terms by means of a classical model and time-dependent calculations on model one-electron systems [2,3]. The picture developed was based on the idea that the symmetric double-well potential formed by the two nuclei is distorted by the external electric field. For small internuclear distances R, the electron may oscillate between the two wells. If R increases, this oscillation will become possible only via tunneling, and finally the electron will be trapped in one of the two wells. If the electron is localized in the lower well, its ionization behavior will be rather similar to that of an atomic electron, since it has to overcome the outer barrier (lowered by the electric field) by means of tunneling or over-barrier escape. However, if the electron is localized in the upper well, ionization by an escape through the inner barrier becomes possible, once a certain value of R is reached. Within a specific R range, tunneling through the inner barrier will be very efficient, and thus an enhanced ionization rate may be observed.

In a static field that is turned on in a sufficiently adiabatic way, the electron will, however, always be in the lower well. On the other hand, in a laser field the direction of the electric field changes, and thus what has been the lower well in one half of the laser cycle will become the upper well in the other half. With this idea in mind, it was emphasized in [2,3] that enhanced ionization depends critically on the time depen-

dence of the electric field, requiring a sufficiently high frequency in order to allow trapping of the electron in the upper well.

More recently, a number of fully three-dimensional *ab initio* calculations for H_2^+ have been presented, considering the case of a static electric field as well as a time-dependent (laser) field. Two approaches based on the complex-scaling method yielded adiabatic static-field ionization rates for the ground (σ_g) and the upper (σ_u) electronic state of H_2^+ that are in very good agreement with each other [4,5]. While the σ_g state did not show any trace of enhanced ionization, the σ_u state exhibited a multipeak structure that was explained by field-induced avoided crossings with other electronic states that in the field-free case are energetically well separated from the σ_u state. Based on this result it is concluded in [5] that population of the σ_u state is required in order to observe enhanced ionization. In a time-dependent field that oscillates too fast for the localized wave function to follow adiabatically, the system will always be in a superposition of the σ_g and the σ_u state, and thus enhanced ionization can occur. This result agrees with the conclusion from the above-mentioned classical picture (in the sense that a time-dependent field is required for enhanced ionization).

To the author's knowledge, so far only one attempt has been made to investigate the possibility of enhanced ionization in the case of a many-electron neutral molecule [6]. In that work a one-dimensional model of H_2 (using softened Coulomb potentials) was investigated and indications for enhanced ionization were found. A fully correlated, three-dimensional (3D) calculation at least for the simplest neutral many-electron molecule (H_2) seems thus to be very timely, and this has now been done by means of a numerical approach developed in this work. The investigation is presently limited to the case of a static electric field parallel to the molecular axis. However, the complete nonrelativistic Hamiltonian describing an H_2 molecule (within the Born-Oppenheimer approximation) in an electric field is diagonalized in a basis spanned by explicitly correlated two-electron wave functions expressed in prolate spheroidal coordinates, allowing a very efficient treatment of electron-electron correlation. The matrix elements of the molecular Hamiltonian (without the field) are calculated with the aid of a computer code written by Kołos and collaborators. The remaining matrix elements steming from the interaction with the electric field are calculated through an extension to the code. The
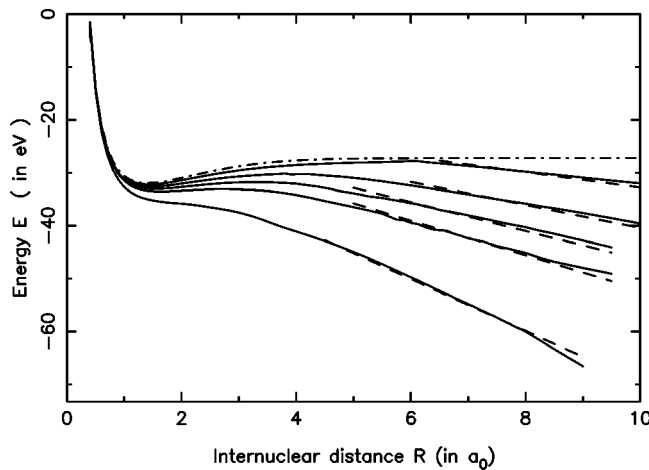
FIG. 1. Adiabatic ground-state potential curve of H_2 in a static electric field for different field strengths, $F = 0.18$, 0.12, 0.10, 0.08, and 0.05338 a.u. (solid lines from bottom to top). Also shown are the field-free curve (chain) and the curves resulting from a simple classical model (dashed).

metastability of the electronic states with respect to autoionization is handled by means of the complex-scaling method. The implementation of this method for diatomic two-electron molecules (in the field-free case) has been described previously [7]. The diagonalization of the complex-scaled Hamiltonian matrix yields directly the adiabatic potential curves and ionization rates. The ionization yields obtained for H_2 in low-frequency laser fields within the quasistatic approximation and their comparison to rates obtained within the Ammosov-Delone-Krainov model (ADK) [8] will be the subject of a forthcoming publication.

It may be noted that the adopted type of basis functions is very efficient for describing two-electron diatomic molecules. In fact, the most accurate Born-Oppenheimer calculations for H_2 existing so far are based on the same *ansatz*. The final results of the present work have been obtained with three 400-term basis sets that showed highest stability in different but overlapping regimes of R. The field-free ground-state potential curve obtained this way agrees with the most accurate one within 10^{-5} eV. This does, of course, not guarantee the same accuracy for the results obtained for H_2 in an external field, but it demonstrates the ability of the method, limited only by the finiteness of the basis. The results presented in this work could certainly be improved on a quantitative level by means of more elaborate basis-set optimization, but the important features on which the following discussion is based were all reproduced with any of the basis sets adopted. In fact, in most cases even the quantitative agreement was very good.

In Fig. 1 the adiabatic ground-state potential curve of H_2 is presented for a number of different field strengths F (1 a.u. $\simeq 5.14 \times 10^{11}$ V/m). For comparison, also the field-free potential curve is given. Qualitatively, the results look rather similar to the ones obtained for H_2^+. One observes a Stark shift, but most importantly the potential curves bend down for increasing values of R, with an increasing slope for increasing field strength. Evidently, the molecular bond will
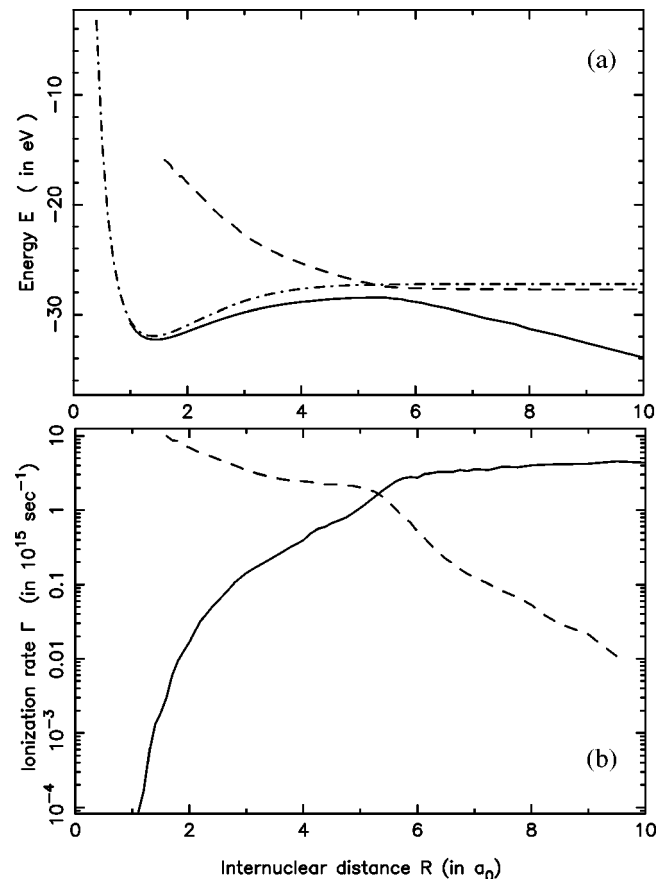

FIG. 2. Adiabatic potential curves (a) and ionization rates (b) for the ground (solid) and one excited state (dashed) of H_2 in a static field $F = 0.06$ a.u. [For comparison, also the field-free potential curve (chain) is shown.]

be softened, and in the case of the strongest field shown, the ground-state potential does not support any vibrational bound state. In the case of H_2^+ this effect was explained by the fact that the σ_g and σ_u states that are degenerate in the limit $R \to \infty$ are coupled to each other by the field [9]. Due to the degeneracy, the coupling matrix element diverges in that limit, which leads to an increasing repulsion of the two levels for $R \to \infty$. While the state where the electron is localized in the lower well will tend to $-\infty$ (and thus bend downwards), the state where the electron is localized in the upper well will tend to $+\infty$ (and thus bend upwards). In a classical picture, these two cases correspond to the situation where H_2^+ dissociates in such a way that the positively charged proton moves parallel or antiparallel with respect to the external potential.

As was pointed out in [9,6], the situation is rather different for H_2, since the state being degenerate to the ground state for $R \to \infty$ is a triplet state, and thus both states will not be coupled by the field (if spin-orbit coupling is ignored). Why should then the ground-state of H_2 that corresponds to dissociation into two neutral fragments be so strongly perturbed by the field? An answer is provided by Fig. 2(a), where not only the ground-state potential curve, but also that of the lowest-lying excited state is plotted. An avoided crossing of these two *adiabatic* potential curves at $R \simeq 5.3\,a_0$ is
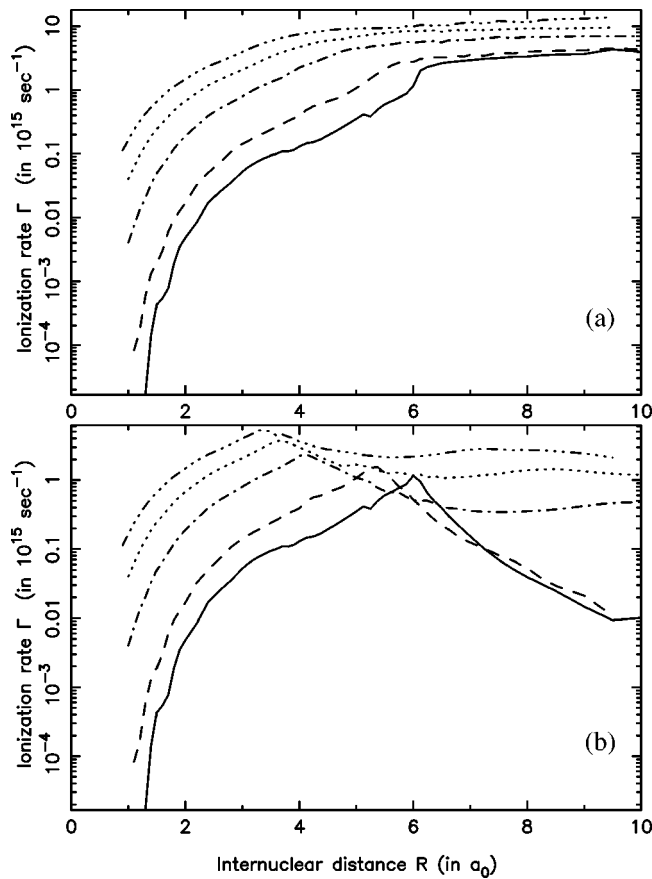
FIG. 3. Adiabatic (a) and diabatic (b) ionization rates of the H_2 ground state for different field strengths [$F = 0.053\,38$ (solid), 0.06 (dashed), 0.08 (chain), 0.10 (dotted), and 0.12 a.u. (dash-dotted)].

FIG. 4. Diabatic ionization rate for $F = 0.053\,38$ a.u. obtained in the present 3D calculation (solid) compared to the rate obtained in a 1D model calculation (chain) [6].

visible. The shown adiabatic continuation beyond the avoided crossing corresponds to an exchange of the character of the two states. On the other hand, the *diabatic*, i.e., the character conserving, continuation of the ground-state potential curve corresponds (beyond the avoided crossing) to the dashed line that in fact follows rather closely the field-free potential curve. (The deviation from it is due to the Stark shift caused by the polarizability of the system.) The origin of the (avoided) curve crossing is due to the fact that the ground-state potential itself is only weakly perturbed by the interaction with the electric field, but the excited state that dissociates into the ionic fragments H^+ and H^- forms a dipole. Thus the two states (forming a dipole along or opposite to the field vector) will exhibit a strong coupling and tend to $\pm\infty$ for $R\to\infty$. The one tending to $-\infty$ is responsible for the avoided crossing shown in Fig. 2(a). At large R the potential curve of that state should be dominated by the energy of a dipole in a field, i.e., by $E = -FR + c$ where c is some constant. In order to support this interpretation, the straight lines predicted by this simple model are also plotted in Fig. 1. The agreement is certainly convincing.

In Fig. 2(b) the ionization rate of the ground and the excited state is given in the adiabatic limit. It is important to realize that the avoided crossing of the potential curves corresponds to a true crossing of the ionization rates and *vice versa* (cf. [4]). In the adiabatic limit, i.e., if the system passes
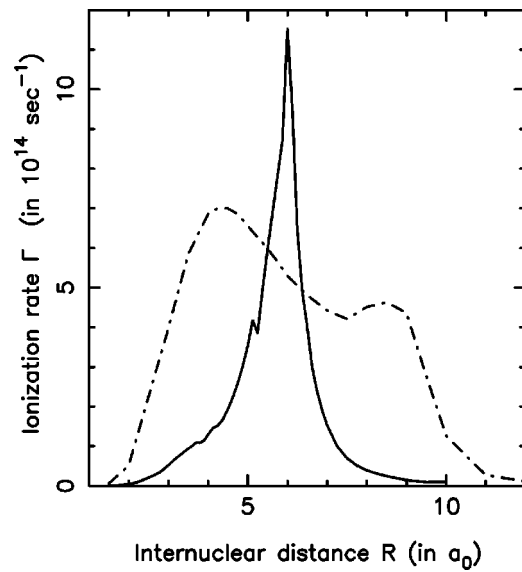
the crossing region infinitesimally slowly, the system will have time to follow the energetically favored curve by changing character (from the neutral to the ionic dissociation limit). With this change it will take over the ionization rate of the ionic system that is large due to the low stability of H^-. In the diabatic limit, the system will, however, not have time to change character and thus regain its own ionization rate, once the coupling region has been passed.

In Fig. 3(a) and 3(b) the influence of the field strength on the ionization rates of the ground state is shown in the adiabatic and diabatic limits, respectively. In the adiabatic limit no enhanced ionization, i.e., no peak in the ionization rate, can be observed. In the case of weaker fields a step is visible that is due to the fact that the (avoided) crossing occurs between two curves with a relatively small angle in between, yielding a very narrow crossing. It is important to realize that such a step may already be sufficient to explain a narrow kinetic-energy distribution observed in a Coulomb-explosion experiment. A detailed simulation also including the nuclear motion would be required to answer this question for a specific experimental situation. In the diabatic limit, on the other hand, the clear signature of enhanced ionization is present for all values of F considered in this work. As in the adiabatic case, this enhancement is most pronounced in the case of the weaker fields. The internuclear distance R at which the ionization rate is peaked shifts to smaller values of R for increasing field strengths [Fig. 3(b)]. This is simply due to the larger slope of the excited-state potential curve induced by a stronger field, which in turn leads to an earlier curve crossing with the ground-state potential curve (cf. Fig. 1).

Finally, in Fig. 4 the diabatic ionization rate is compared to the result obtained with a one-dimensional (1D) model in [6]. While the order of magnitude of the maximum ionization rate is in reasonable agreement, there are two fundamental differences. The presently predicted peak is much narrower and it does not support any double-peak structure (the

minor peak on the shoulder is only due to numerical inaccuracies). According to the present interpretation, a second peak could only be explained by the occurrence of a second (avoided) crossing. Following the ground-state potential curve diabatically, it is of course possible that another, even higher-lying state (dissociating, e.g., into H^+ and some excited state of H^-) could cross this curve at some larger value of R. The present full calculation does, however, not support a second crossing for $R \lesssim 10\, a_0$. Possibly, the 1D model underestimates the value of R where curve crossings occur.

Considering the present results together with previous ones obtained for H_2^+, a rather *general quantum-mechanical picture* emerges. Enhanced ionization occurs due to curve crossing. In a diatomic molecular ion this crossing occurs for the ground state due to the coupling with the first excited state, since within an external field these two states correspond to the situation where the ionic dissociation fragment moves either parallel or antiparallel to the field. In a (covalent) neutral diatomic molecule the diabatic ground-state potential curve is nearly unaffected by the field (only shifted by the Stark shift), but it will be crossed by those potential curves of the excited states that dissociate into ionic fragments. Similar to the case of the ground states of molecular ions, there should always be a couple of ionic states where in a field one will tend to $-\infty$ and the other to $+\infty$, representing the possibilities of the dipole to be oriented along or opposite to the external field.

According to the present interpretation, enhanced ionization will only be present, if the molecular system moves sufficiently fast over the crossing. In the adiabatic limit enhanced ionization will not occur, at least not in the sense of a sharp maximum in the ionization rate. In previous discussions mainly the (a)diabaticity induced by the external field

had been considered, and its importance was already given within the classical model. There exists, however, a second important parameter, the velocity of the nuclei. While in a laser field both parameters have to be taken into account, in a static field only the second parameter plays a role, if the turn-on and -off process is ignored. This second parameter seems to have been overlooked in previous discussions of possible enhanced ionization in H_2^+ within a static field.

On the basis of the present work it is also possible to elucidate a very recent observation made for H_2^+ in [10] that could not be explained by the authors. In that work it was reported that the maximum of the enhanced ionization rate, R_{max}, depends on the field strength F in such a way that the product $R_{max}F$ is approximately constant. From the interpretation given above, it is clear that the maximum of the enhanced ionization rate will shift to smaller values of R as the field is increased, and that this effect is directly related to the slope of the upper curve that in turn is proportional to F.

The experimental observability of enhanced ionization of H_2 itself may be difficult, since it occurs at rather large internuclear distances, and the molecule may ionize long before it reaches such a value. Nevertheless, one may speculate on its observability, e.g., by starting from a highly excited vibrational state, or by trying to observe the reduced ionization that should occur for the electronically excited state. Alternatively, the investigation via laser-assisted scattering of two neutral hydrogen atoms may be contemplated. Considering the generality of this phenomenon according to the present interpretation, one may, however, search for another molecular system where better conditions for experimental detection may exist.

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