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Behavior of molecular hydrogen exposed to strong dc, ac, or low-frequency laser fields. I. Bond softening and enhanced ionization

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A three-dimensional, fully correlated *ab initio* method for calculating the ionization rates and Stark shifts of molecular hydrogen oriented parallel to an external electric or low-frequency electromagnetic field is presented. With its aid, the occurrence of bond softening and enhanced ionization in H_2 is investigated. Based on a simple quantum-mechanical explanation for those effects, their occurrence is also predicted for any neutral covalently bound molecule. The *ab initio* results are used to investigate the applicability of simpler numerical models for predicting those phenomena in larger molecules.

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I. INTRODUCTION

Atoms or molecules exposed to very strong electric or electromagnetic fields will usually undergo ionization which in the molecular case may be accompanied or followed by dissociation. The full understanding and quantitative modeling of the corresponding ionization rates is therefore important in all experiments in which strong fields are applied. Nowadays, very strong electric (more accurately electromagnetic) fields are produced with the aid of lasers, but also scanning-tunneling microscopy as a source for strong electric fields should be mentioned. Since the efficiency of high-order harmonic generation appears to be limited by the ionization process, a prediction of suitable materials for high-order harmonic generation requires an accurate knowledge of the ionization rates. The same is valid for the understanding of e.g. Coulomb explosion, i.e. the dissociation of molecules in laser fields as a consequence of their field-induced stripping from electrons (see e.g., Ref. [1]).

Although a static dc (or time-dependent ac) electric field and a time-dependent electromagnetic (laser) field are fundamentally different objects, it turned out that the effects of a strong low-frequency laser are very similar to those of an ac field. If the frequency of the laser is small compared to the inherent time scale of the system exposed to it, the system seems to behave as it would be exposed to a slowly varying dc field, i.e. an ac field. This is the basis of the so-called quasistatic approximation. The parameter that indicates whether the quasistatic regime is reached is the Keldysh parameter $\gamma=\omega\sqrt{2I_P}/F$ with the frequency ω and the field strength F of the laser and the ionization potential I_P of the atomic or molecular system [2]. The quasistatic approximation is supposed to be applicable in the low-frequency high-intensity regime $(\gamma\ll 1)$.

For the quasistatic model to be useful, it is required that static ionization rates are available. Besides atomic hydrogen, full *ab initio* calculations of the ionization rate of atomic systems exposed to dc fields are, however, very scarce. Scrinzi *et al.* [3] and Themelis *et al.* [4] have presented *ab initio* dc ionization rates for He, and Sahoo and Ho [5] as well as Themelis and Nicolaides [6] for Li. In the molecular case quantum-mechanical dc ionization rates have been calculated for H_2^+ [7,8] and, as was reported in the preceding *Rapid Communication* [9], it was now also possible to implement a method that allows the full *ab initio* treatment of H_2 molecules exposed to strong dc fields.

One of the interesting aspects of understanding the behavior of molecules in static or quasistatic fields is the prediction of enhanced ionization and bond softening in arbitrary covalent and neutral molecules [9,10]. The former of those effects, predicted, analyzed, and discussed on the basis of the static ionization rates obtained with the method developed in the present work was shortly thereafter also confirmed in a time-dependent calculation [11]. Noteworthy, based on a 40 years old prediction [12,13] it was assumed that bond softening will not occur for neutral molecules and first indications of enhanced ionization for H_2 were only due to a one-dimensional model calculation [14]. In the present work both effects are investigated on the basis of a three-dimensional, fully-correlated *ab initio* calculation. The new theoretical and numerical approach allowing for this investigation is also presented. Due to its numerical demands, this method cannot easily be extended to larger molecules. Therefore, the possibility of using simplified numerical approaches is discussed by comparing the results obtained for H_2 using either the full or simplified numerical methods.

After describing the theory and computational method in the following section, the effects of bond softening and enhanced ionization in H_2 will be discussed in Sec. III. The paper closes with a conclusion and outlook. Unless otherwise specified, atomic units ($E_h=27.211$ eV, $a_0=5.2918\times10^{-11}$ m and $\hbar=e=m_e=1.0$) are used in this paper.

II. THEORY AND COMPUTATIONAL DETAILS

If an atomic or molecular system is exposed to an electric field, the (static and homogeneous) electric field adds a scalar potential to the Hamiltonian. For example, a field along the z axis leads to the Hamiltonian (in atomic units)

$$\hat{H}=\hat{H}_0+F\left(\sum_{N=1}^{N_n} Z_N z_N-\sum_{n=1}^{N_e} z_n\right), \tag{1}$$

where $\hat{H}_0$ is the field-free Hamiltonian describing the atom or molecule with N_n nuclei (with charge Z_N) and N_e elec-

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*Electronic address: Alejandro.Saenz@uni-konstanz.de trons. F is the field strength (1 a.u. corresponds to about 5.142×10^{11} V/m). In writing Eq. (1) it is assumed that a nonrelativistic description for the interaction with the field is applicable. This should be true for the fields considered in this work.

Before presenting the newly developed computational method, it is interesting to briefly comment on the finite-field methods that are implemented in a number of standard quantum chemistry codes. In a weak field, perturbation theory is applicable. In this case the first-order correction obtained with perturbation theory vanishes for atomic or molecular systems with no permanent dipole moment, while those having a permanent dipole moment show a linear Stark effect, i.e., the energy correction varies linearly with the field strength. The second-order correction depends quadratically on the field strength, the proportionality constant is the polarizability α_{zz} (times a factor $-1/2$). The third-order correction is then proportional to the hyperpolarizability γ_{zzz} etc. The calculation of the polarizability, hyperpolarizability etc. may be performed by an explicit calculation of the corresponding expansions of perturbation theory, which in principle requires a summation over the infinite number of field-free eigenstates of the atom or molecule. Alternatively, the polarizability (and hyperpolarizability) can be obtained from the response of the molecular system to an external electric field. In this case, Eq. (1) is solved directly and the resulting energies may be fitted to a polynomial in the field strength F; thus revealing the polarizability, hyperpolarizability etc. Since the operator(s) z (x or y) is (are) contained in many quantum-chemistry codes (for the calculation of dipole moments), it is relatively simple to set up Eq. (1) and thus to obtain the in-field eigenstates (or the coefficients of the perturbation series). This is the basis of the so-called finite-field methods implemented in many standard quantum-chemistry codes.

Although it may appear that finite-field calculations already provide a solution for describing atomic or molecular systems in electric fields of arbitrary field strengths, this is not the case. The problem is that a standard quantum-chemistry calculation based on square-integrable basis functions is not appropriate, since a nonzero field allows the electrons to leave the molecule via tunneling, or for even stronger fields by a passing over the suppressed molecular potential barrier. Although, strictly speaking, even an infinitesimally small electric field (with sufficient spatial extent) leads to a pure continuous spectrum (in which the original bound states are embedded as autoionizing states), the width of strongly bound field-free states is very small for weak fields. In this case a calculation that ignores the field-induced widths (using square-integrable basis functions) of the ground and low-lying excited states is expected to give reasonable results. Naturally, the tunneling probability depends on the depth of the potential felt by the electrons, and thus strongly bound field-free states will have much smaller ionization rates than weakly bound ones. Whereas the ground state of a molecule may still be well described when ignoring the width induced by the electric field, this may not be the case for highly excited or Rydberg states.

After the prediction of tunneling ionization in electric fields a number of methods have been developed to treat this effect numerically, but most of them were very difficult to be extended to systems beyond the hydrogen atom (or hydrogen-like one-electron ions). The metastability of the in-field atomic or molecular states due to the induced tunnel-ionization probability can, for example, be taken into account very efficiently within the complex-scaling method [15–19], as was demonstrated first numerically in the case of one-electron atoms in an external field [20] and then also demonstrated mathematically for arbitrary atomic systems exposed to electric fields [21]. An important feature of the complex-scaling method is that it does not only give the correct position of the resonance, but at the same time it gives also its width. Complex-scaling has recently been used to obtain static-field ionization rates of He [3], and simplified related (though mathematically so far less well-funded) methods were used for calculating the field-induced ionization rates of He and Li [4–6].

In the complex-scaling method the Hamiltonian $\hat{H}$ is transformed into a complex-scaled Hamiltonian $\hat{H}(\theta)$ by multiplying the radial coordinates by $e^{i\theta}$ where θ is an (in principle) arbitrary positive real number smaller than $\pi/4$. This transformation allows an analytically correct continuation of the spectrum of the Hamiltonian into the complex plane, provided the Hamiltonian belongs to the group of dilatation analytic operators. This is the case for field-free atomic and molecular Hamiltonians, and also for such systems exposed to an external electric field [21]. As a result of the transformation, the continuum spectrum of the Hamiltonian is modified, while the bound spectrum remains unchanged. Resonant states (like autoionizing or predissociative states) will obtain a fixed, but complex energy, provided θ is chosen sufficiently large so that they are uncovered by the underlying continuum. In this case the real part of the complex energy eigenvalue corresponds to the position of the resonance, while the width Γ of the state can be obtained from the imaginary part of the energy E via $\Gamma=-2\,\mathrm{Im}\{E\}$. In a practical calculation, a finite basis set is used, and thus depending on the quality of the basis set the resonances will show some θ dependence. In this case a sequence of calculations is performed in which θ is varied. The complex energy E_{res} (and thus position and width) of the resonance is then obtained by searching for the most stable energy and thus the minimum of $dE_{\mathrm{res}}(\theta)/d\theta$.

In the present approach, it is assumed that the Born-Oppenheimer approximation as well as a nonrelativistic description is applicable for treating a two-electron diatomic molecule in an external electric field. The present work is also limited to the case that the electric field is oriented parallel to the internuclear axis. In this situation, both the spin symmetry (singlet or triplet) and the total angular momentum Λ around the internuclear axis (Σ, Π, etc. symmetry) are good quantum numbers. However, even in the case of a homonuclear molecule like H_2 the parity (*gerade/ungerade* symmetry) will be destroyed by the external field. Therefore, homonuclear or heteronuclear molecules in a field are with respect to symmetry equivalent to heteronuclear molecules in the field-free case. Consequently, one should expect that any basis that is able to accurately describe heteronuclear diatomic molecules in the field-free case is suitable for the problem of describing an arbitrary diatomic molecule in an electric field.

A very successful type of basis functions has been introduced for heteroatomic diatomic molecules by Kołos [22]. This basis is expressed in the prolate spheroidal coordinate system $\{1 \leqslant \xi < \infty, -1 \leqslant \eta \leqslant 1, 0 \leqslant \phi \leqslant 2\pi\}$ defined by

$$\xi_j = \frac{r_{j,A} + r_{j,B}}{R}, \quad \eta_j = \frac{r_{j,A} - r_{j,B}}{R}, \quad \text{and} \quad \phi_j, \tag{2}$$

where $j = 1,2$ denotes one of the two electrons, A,B are the two nuclei, $R = r_{A,B}$ is the internuclear distance, ϕ is the angle around the internuclear axis, and $r_{m,n} = |\vec{r}_m - \vec{r}_n|$. A single basis function ψ_k that is adapted to $^1\Sigma$ symmetry is given by

$$\psi_k(\vec{r}_1, \vec{r}_2; R) = (1 + \mathcal{P}_{1,2}) \left(\frac{2 r_{1,2}}{R} \right)^{\mu_k} \times \xi_1^{p_k} \eta_1^{q_k} \xi_2^{\bar{p}_k} \eta_2^{\bar{q}_k} e^{-\alpha \xi_1 - \bar{\alpha} \xi_2 + \beta \eta_1 + \bar{\beta} \eta_2}, \tag{3}$$

where $\mathcal{P}_{1,2}$ is the permutation operator that interchanges the coordinates of the two electrons. A basis set of dimension N is then defined by a specification of the exponents $\alpha, \bar{\alpha}, \beta, \bar{\beta}$ (identical for all basis functions) and N sets $\{\mu_k; p_k, q_k, \bar{p}_k, \bar{q}_k\}$ of integers. In the present work four basis sets containing $N = 400$ integer sets and four different sets of partly constant, partly R-dependent exponents $\alpha, \bar{\alpha}, \beta, \bar{\beta}$ have been used to obtain the results and to check their reliability. Convergence with respect to the size of the basis was also investigated by comparing the results at selected values of R with those obtained with 200 basis functions only. Note that a very efficient inclusion of electron-electron correlation is achieved by the adopted type of basis functions, since they depend explicitly on the interelectronic distance $r_{1,2}$.

Although the complete Hamiltonian describing a molecule is dilatation analytic, i.e., it can be continued into the complex plane using the complex-scaling method, this is not the case for the molecular Hamiltonian when expressed in the Born-Oppenheimer approximation. This is true even in the field-free case. As a consequence, the standard complex-scaling method cannot be applied. A solution to this problem is provided by the method of exterior complex scaling where only part of the radial coordinate space is complex dilated [23]. Usually, this is mathematically exact but discontinuous scaling is very difficult to implement in a numerically stable manner, and therefore smooth-exterior scaling [24] and the related, though mathematically less well-funded complex-absorbing potential method [25] were introduced. It was realized in Ref. [26] that the prolate spheroidal coordinate system allows, however, a straightforward implementation of exterior complex scaling, since it can be achieved by transforming the electronic Hamiltonian $\hat{H}(\xi, \eta, \phi)$ into $\hat{H}(e^{i\theta}\xi, \eta, \phi)$. In Ref. [27] this procedure was then implemented in connection with the two-electron diatomic-molecule electronic-structure code of Kołos *et al.* In order to avoid the implementation of new (complex) integrals, a numerical trick is adopted. Using the fact that a scaling of the Hamiltonian can be substituted by an inverse scaling of the basis functions [28–30] it is possible to obtain the matrix elements of the complex-scaled Hamiltonian by an inverse scaling of the basis functions. Instead of calculating the matrix elements of the complex-scaled basis functions directly, which would still be a formidable task, they are calculated for a number of real-scaling factors. Then every Hamiltonian matrix element is fitted by a polynomial in the real-scaling factor. This polynomial is used for obtaining the Hamiltonian matrix elements for complex-scaling factors. The correct implementation has been tested in a number of calculations, including autoionizing states and single as well as multiphoton ionization spectra. That code was now extended for treating diatomic two-electron molecules in an electric field. It is interesting to note that a similar approach has been used in the first fully three-dimensional treatments describing H_2^+ in an external field [7,8].

After the calculation of the matrix elements of the complex-scaled Hamiltonian $\hat{H}(e^{i\theta}\xi, \eta, \phi)$ in the explicitly correlated basis defined in Eq. (3), the complex energies and eigenvectors of the resulting complex symmetric Hamiltonian matrix are obtained by matrix diagonalization. Since in an electric field no truly atomic or molecular bound state exists, all field-free bound states turn into resonances, if the field has nonzero strength. There is an evident numerical problem, if the width of a state is very small, since in that case the numerical precision of the evaluation of the matrix elements (this includes the finite precision in the integration on the real axis and the numerical extrapolation into the complex plane) and of the matrix diagonalization is limited. Practical experience shows that the basis-set quality is often the most limiting parameter and better (more complete) basis sets allow to determine the width of narrower resonances. In the present case, the smallest widths that could reliably be determined were of the order of about 10^{-5} a.u. when using double-precision accuracy in the FORTRAN codes. Of course, this problem affects mainly the width, but not the position of narrow resonances that is typically very precisely determined. In the context of the present work the width of the electronic ground state could therefore be determined for field intensities starting from about 0.05 a.u. In the case of electronically excited states that are weaklier bound than the ground state, it is of course possible to calculate the field-induced width for correspondingly smaller field strengths. In order to determine the position and width of the electronic states the complex-scaling angle θ was usually varied in between 0 and 0.70 rad in steps of 0.01 rad. The resonant trajectories were then graphically inspected, and the minimum of the θ dependence numerically determined by a finite-differencing scheme. It is important to note that the qualitative findings of the present work (bond softening, enhanced ionization, etc.) are all reproduced when using any of the basis sets. In most cases, even the quantitative agreement between the results obtained with all different basis sets, especially those containing 400 basis functions, is very good.

In the present approach, the complex-scaled wave functions $\Psi_n^{\theta,F}(\vec{r}_1,\vec{r}_2;R)$ describing the electronic part of state n exposed to a field with strength F are obtained as linear combinations of the basis functions [cf. Eq. (3)]

$$\Psi_n^{\theta,F}(\vec{r}_1,\vec{r}_2;R)=\sum_{k=1}^{N} c_{n,k}^{\theta,F}\psi_k(\vec{r}_1,\vec{r}_2;R), \tag{4}$$

where the (in general) complex coefficients $c_{n,k}^{\theta,F}$ result from the matrix diagonalization. The wave function expressed this way cannot easily be related to the one that is obtained for the field-free case. Therefore, in a second approach the complex-scaled field-free wave functions are calculated in a first step, and then the operator describing the field is added to the resulting Hamiltonian. Now, the electronic wave functions are given by

$$\Psi_n^{\theta,F}(\vec{r}_1,\vec{r}_2;R)=\sum_{k=1}^{N} \tilde{c}_{n,k}^{\theta,F}\Psi_k^{\theta,F=0}(\vec{r}_1,\vec{r}_2;R). \tag{5}$$

This approach allows a direct analysis of the electronic in-field wave functions in terms of the field-free wave functions.

It is important to realize the different time scales involved in the interaction of a molecule with an external field. In the case of an atom, the different time scales are set by the motion of the electrons and the time variation of the external field. The latter may be due to the turn-on, switch-off, or a time-dependent field-strength variation in the case of a dc field or additionally due to the time periodicity in the case of an ac field. In a laser pulse, the electric-field component varies depending on the pulse envelope and especially for linearly polarized lasers also on the photon frequency. Ignoring the envelope of the pulse, the relative time scales of the photon frequency and the electronic (tunneling) motion divides the *quasistatic* from the *multiphoton regime*, as was discussed above. If the field intensity increases fast on the time scale of electronic motion, but remains on this high value for a long time compared to it, the *limit of a sudden turn-on* is reached [10]. In the case of an optical laser this would require elliptical or circular polarization. In the molecular case an additional time scale is induced by nuclear motion. In the high-frequency multiphoton limit vertical transitions are expected, perhaps with some (usually small) corrections due to nonadiabatic couplings between electrons and nuclei.

In the quasistatic regime, different situations can be envisioned. Since electronic motion is usually faster than nuclear one, the sudden turn-on limit (fast intensity rise followed by constant intensity) will be similar for atoms and molecules. If the field approaches the intensity maximum slowly compared to electronic and nuclear motion, electrons and nuclei can follow adiabatically and populate the adiabatic in-field state. A further complication arises, if the field induces avoided crossings between adiabatic potential curves and if the nuclei have the possibility to reach the internuclear-distance range of this crossing. In this case, it depends on the velocity of the nuclei whether the system will pass adiabatically over the avoided crossing (remaining on the energetically favored adiabatic potential curve, but changing the electronic character) or diabatically (keeping the electronic character but switching the adiabatic state). The former situation may be called *fully adiabatic limit*, and the latter one *vibrationally diabatic limit*. Of course, the finite vibrational motion (already due to zero-point vibration) yields a situation that lies somewhere in between those two limits. There is, however, also another limit possible. In this case, the field variation is slow on the time scale of molecular electrons, but fast on the one of the nuclei. The electrons will thus form the adiabatic in-field potential curves and ionize with the adiabatic field ionization rates, but the nuclei remain practically frozen during the change of the field. If after the rise the field intensity remains constant for a time interval that is long on the time scale of nuclear motion, the field-free nuclear wave packet will propagate on the adiabatic in-field potential curves. This situation corresponds to the turn on of a dc field or a rise of the intensity of a circularly polarized laser on the time scale in between the ones of electronic and nuclear motion. This situation may be called *frozen-nuclei limit*. In the case of a linearly polarized laser with, e.g., optical frequency the field will reach its intensity maxima on a time scale that is slow with respect to the electronic motion and fast with respect to the nuclear one, but it will persist only for a very short time. Then, the nuclei have practically no time to move, and only electronic excitation (ionization) will occur (*non-moving-nuclei limit*). The frozen- or non-moving-nuclei limits should not be confused with the fixed-nuclei approximation in which the ionization rate is obtained at a fixed internuclear distance defined by the minimum of the field-free ground-state potential curve.

The solution of the electronic part of the Born-Oppenheimer Hamiltonian gives (by construction) adiabatic potential curves. Nonadiabatic effects are especially important, if nuclear motion occurs on a potential surface that is strongly coupled to one or more other potential surfaces. Since field-induced avoided crossings play an important rôle in this work, it is of interest to consider also diabatic potential curves. Their calculation is, however, a nontrivial task, and thus one often adopts schemes that allow to transform the adiabatic curves into quasidiabatic ones; a procedure that is, however, not uniquely defined. Since it is the external field that induces the avoided crossings, the following approach was implemented in order to obtain quasidiabatic ground-state potential curves in the field. The wave functions are obtained by expressing them in terms of field-free wave functions [Eq. (5)]. However, instead of diagonalizing the full Hamiltonian, the largest off-diagonal coupling matrix element of the field-free ground state with the remaining states is set to zero. In this way the field-induced avoided crossing turns into a true crossing, but the Stark shift (and interaction with higher-lying states) should still be included in the ground-state potential curve. Noteworthy, the ignored off-diagonal element is exactly the (R-dependent) coupling matrix element that is required to, e.g., estimate within the Landau-Zener model the probability that a certain portion of a nuclear wave packet passing over the crossing will follow either the diabatic or the adiabatic continuation of the potential curve.

The complete, fully adiabatic molecular wave function $\Phi^{\theta,F}_{n,v,J}$ describing both electronic and nuclear motion (and separating off the overall translational motion) is obtained within the Born-Oppenheimer approximation as a product of an electronic ($\Psi^{\theta,F}_{n}$) and a rovibrational nuclear ($\Upsilon^{n,F}_{v,J}$) wave function,

$$\Phi^{\theta,F}_{n,v,J}(\vec{r}_1,\vec{r}_2,\vec{R})=\Psi^{\theta,F}_{n}(\vec{r}_1,\vec{r}_2;R)\Upsilon^{n,F}_{v,J}(\vec{R}). \qquad (6)$$

In the present study the electronic states are only calculated for the case of a parallel orientation of the internuclear axis and the field, as should be experimentally relevant, if it is assumed that at least light molecules align in a field in this way due to the different polarizabilities along the parallel and the perpendicular direction. Instead of solving the three-dimensional Schrödinger equation describing the rovibrational motion of a diatomic molecule, only the simplified rotationless (quasi-one-dimensional) equation

$$\left[-\frac{1}{2\mu}\frac{d^2}{dR^2}+V^{\theta,F}_{n}(R)\right]\tilde{\Upsilon}^{n,F}_{v}(R)=E^{\theta,F}_{n,v}\tilde{\Upsilon}^{n,F}_{v}(R) \qquad (7)$$

is solved for obtaining the complete molecular wave function in a dc field. While μ is the reduced mass of the molecule, $V^{\theta,F}_{n}(R)$ is the now complex potential curve of the electronic state n in a field with strength F. $E^{\theta,F}_{n,v}$ is the total energy of the molecule in the field (within this model), the real part being the energy position and the imaginary part $\mathrm{Im}\{E^{\theta,F}_{n,v}\}$ being directly proportional to the width in the fully adiabatic limit, $\Gamma^{\mathrm{adiab}}_{n,v}=-2\,\mathrm{Im}\{E^{\theta,F}_{n,v}\}$ (cf. above). Equation (7) is solved by expanding the nuclear wave functions in terms of B-spline basis functions [31]. In this way the Schrödinger equation is transformed into a matrix eigenvalue problem. Typically 202 B splines of order 8 have been used in the calculations. Mostly, they span the internuclear-distance interval from 0 to $10a_0$. In some cases it was, however, necessary to vary or lower the upper bound in order to identify the vibrational bound states in the predissociative tunneling continuum created due to bond softening in the field. In all cases, a linear knot sequence was chosen for the B splines.

In order to calculate the ionization rate in the vibrationally diabatic limit, Eq. (7) would have to be solved inserting the (quasi) diabatic in-field potential curve for $V^{\theta,F}_{n}(R)$. As is discussed below, it turns out that the quasidiabatic curves obtained by setting the largest coupling to zero are very similar to the field-free ones, except that they contain some Stark shift and some oscillations due to indirect couplings to higher-lying states. Solving the vibrational Hamiltonian using an electronic potential that contains spurious oscillations is not senseful. To avoid this problem, the curve would have to be smoothened. Since there is no unique way for performing this smoothing, and it will anyhow contain some approximation, one could instead use the field-free potential curve as a real part of $V^{\theta,F}_{n}(R)$, i.e., $\mathrm{Re}\{V^{\theta,F=0}_{n}(R)\}$.

The ionization rates in the frozen-nuclei- and the nonmoving-nuclei limits are necessarily the same. The rate $\Gamma^{\mathrm{froz}}_{n,v}$ is obtained from solving Eq. (7) using the field-free potential curve $V^{\theta,F=0}_{n}(R)$ to obtain the field-free nuclear wave function $\tilde{\Upsilon}^{n,F=0}_{v}(R)$ and using it together with the adiabatic electronic *ab initio* ionization width $\Gamma^{F}_{n}(R)=-2\,\mathrm{Im}\{V^{\theta,F}_{n}(R)\}$ when solving

$$\Gamma^{\mathrm{froz}}_{n,v}=\int_0^\infty[\tilde{\Upsilon}^{n,F=0}_{v}(R)]^*\Gamma^{F}_{n}(R)\tilde{\Upsilon}^{n,F=0}_{v}(R)\mathrm{d}R. \qquad (8)$$

As is discussed in Ref. [10], the results obtained with Eq. (8) or using the field-free potential curve in Eq. (7) are very similar, if not too high ionization rates (and thus intensities) are considered. Therefore, the vibrationally diabatic ionization rate is very similar to the frozen-nuclei one, if the approximations discussed above are used. No explicitly calculated values in the vibrationally diabatic limit are thus presented in this work, since the approximations made by setting the diabatic in-field potential curve equal to the field-free one appears to result in a larger error than is obtained due to using Eq. (8) instead of Eq. (7).

III. BOND SOFTENING AND ENHANCED IONIZATION

A. Bond softening

Already four decades ago it was predicted, and experimentally confirmed, that the chemical bond in diatomic molecular ions with an odd number of electrons is softened, if an external electric field is applied [12,13]. This phenomenon is due to the fact that the bound electronic ground state of those ions is degenerate with the repulsive first excited state in the limit $R\rightarrow\infty$ (R is the internuclear distance) and this degeneracy is lifted by an electric-field component parallel to the molecular axis. While the effect of bond softening by external electric fields was further explored after its first observation (see e.g. Ref. [32]), the interest in this effect clearly increased about a decade ago, since the intense lasers developed by that time create sufficiently strong electric fields to observe bond softening even for very low-lying vibrational states. Especially the intense CO_2 lasers should fulfill the criteria for applicability of the quasistatic approximation (due to their relatively low frequency) and thus the behavior of molecules in such laser fields should show the same effects as that seen in a static electric field. Bond softening with lasers was then predicted theoretically and observed for $H_2{}^+$ and later on also for HCl^+ [33–35]. In fact, those experiments were performed on the neutral counterparts, but in the interpretation it was assumed that the neutral molecule is first tunnel ionized on the rising edge of the laser pulse. In this ionization process different vibrational states of the molecular ion are populated, the population being assumed to follow a Franck-Condon distribution (which is, however, an erroneous assumption as is discussed in Ref. [31]).

Considering neutral diatomic molecules (or molecular ions with an even number of electrons) the situation should be rather different. As Hiskes pointed out already 40 years ago [12], in that case the electronic ground-state potential curve is degenerate for $R\rightarrow\infty$ with a state of different spin symmetry. For example, the singlet ground state of H_2 is degenerate with the lowest-lying triplet state. Since the external field does not couple those states (at least if relativistic effects are ignored, and even if they are included, the cou-

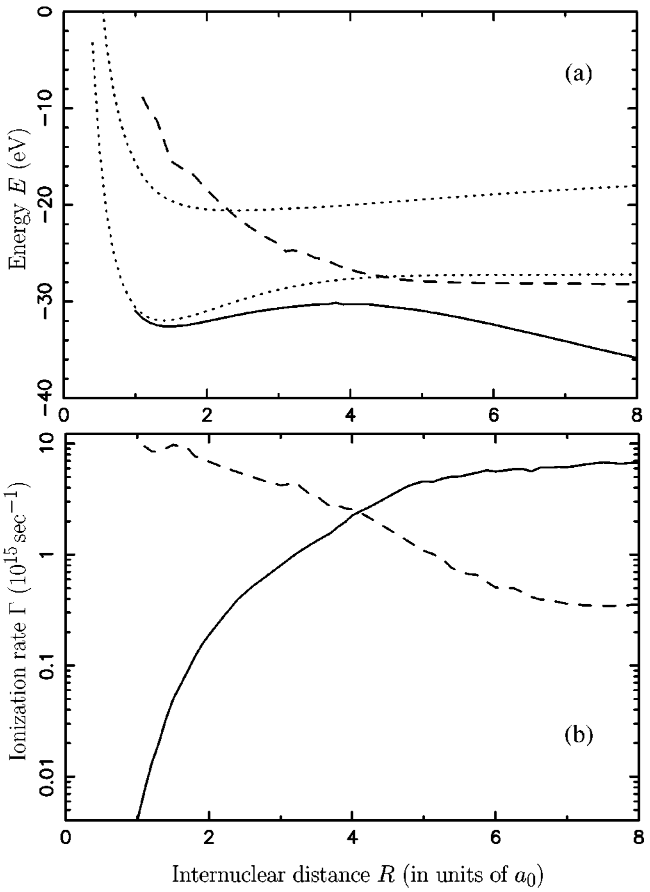

FIG. 1. Adiabatic potential curves (a) and ionization rates (b) for the ground (solid) and one excited state (dashed) of H_2 in an electric field of strength $F = 0.08$ a.u. [For comparison, also the field-free ground ($X^1\Sigma_g^+$) and first excited state ($B^1\Sigma_u^+$) potential curves of $^1\Sigma$ symmetry are shown (dotted).]

pling will be correspondingly weak), Hiskes concluded that the only effect of the electric field on the electronic ground state is to induce some Stark shift. Therefore it was argued that no bond softening occurs in neutral diatomic molecules.

In Fig. 1(a) the two lowest-lying adiabatic $^1\Sigma$ potential curves of H_2 exposed to a static electric field of strength $F = 0.08$ a.u. are shown together with the field-free ones. Clearly, an avoided crossing is observed. Although this finding is in evident contrast to the prediction of Hiskes, it can easily be explained in the following way. H_2, like any covalently bound neutral diatomic molecule, possesses also some (often energetically rather highly lying) state with ionic character, i.e., a state that does not dissociate into two neutral fragments, but into one positively and one negatively charged ionic fragment. While the states dissociating into neutral fragments are only weakly affected by the external field (as predicted by Hiskes), this is not the case for the ionic state. Since this latter state has an increasing dipole moment when R is enlarged, the state which represents dissociation in such a way that the dipole is oriented parallel to the field is energetically very favorable, as its energy behaves (for large R) as $-FR$. For any finite field, the potential curve of this ionic state crosses therefore at some point the ground-state potential curve which is nearly unaffected by the field. Since both states have the same symmetry ($^1\Sigma$), they are coupled and therefore show an avoided crossing. This interpretation is directly supported by Fig. 1(a), since the field-free potential curve agrees for small values of R rather well with the lowest-potential curve in the field, while for large R it is the upper curve in the field that is energetically very close to the field-free ground-state potential curve. This indicates that adiabatically following the lowest potential curve in the field means that one follows a state that switches character when passing the avoided crossing. For small R the ground state in the field has predominantly covalent character, while the adiabatic continuation after the avoided crossing corresponds to a dominantly ionic state and dissociates into H^+ and H^-.

In the opposite extreme of a diabatic dissociation a molecule starting in the electronic ground state will not have the time to change electronic character when passing over the avoided crossing. Therefore, it will follow the upper potential curve, once the region of the avoided crossing has been passed over, and thus it will dissociate into two neutral fragments. For any finite velocity there is a certain probability (which again may be estimated using Landau-Zener theory) that the molecule starting in either the ground or the excited state will dissociate in either of the two dissociation limits, neutral, or ionic dissociation. In an ac or a low-frequency laser field the time variation of the external field induces an additional velocity component and thus an additional parameter that has to be considered when trying to predict the ratio of neutral and ionic dissociation fragments for a specific experiment.

The field-induced avoided crossing implies a suppression of the ground-state potential barrier. In addition, the potential minimum broadens due to the avoided crossing. Those two effects naturally influence the position and number of bound vibrational states supported by the potential well. Highly lying vibrational states become unbound due to the field. Exactly this effect was called bond softening when it was predicted for molecular ions. Again, the velocity of the nuclei plays an important role in the prediction of observable quantities. In the vibrationally diabatic limit, the lower-state potential curve continues beyond the avoided crossing in a very similar way as the field-free one. In this case, bond softening will almost not occur, since the potential curve is basically only deformed by the Stark effect.

In Table I the energy position of the lowest vibrational bound state ($v_0 = 0$) is given as a function of the field strength F. The energies were obtained from solving Eq. (7) using the field-dependent complex adiabatic ground-state potential curves. Due to the Stark shift, the position moves to lower-energy values, if the electric field is turned on. If bond softening should occur in the adiabatic limit, the lowering of the minimum of the potential well has to be smaller than that of the top of the potential barrier. As can be seen from Table I, at $F = 0.053\,38$ a.u. (corresponding to a laser peak intensity of 10^{14} W/cm^2) the minimum is more strongly affected by the field than the top of the potential barrier (the avoided crossing occurs at a too large internuclear distance) and thus the adiabatic in-field potential curve supports in fact more bound vibrational states than the field-free one. However,

TABLE I. Energies E of the first ($v_0 = 0$) and last ($v_{\text{max,ad}}$) bound vibrational state obtained for the electronic ground state of H_2 and for different field strengths F within the fully adiabatic limit. Also shown is the index ($v_{\text{max,froz}}$) of the last bound vibrational state obtained in the frozen-nuclei limit.

F (a.u.)	E_{v_0} (a.u.)	$E_{v_{\text{max,ad}}}$ (a.u.)	$v_{\text{max,ad}}$	$v_{\text{max,froz}}$
0.0	−1.164545	−1.000675	14	14
0.05338	−1.174689	−1.017666	16	10
0.06	−1.177572	−1.050107	11	7
0.08	−1.189281	−1.115217	6	3
0.10	−1.205617	−1.169065	3	
0.12	−1.225239	−1.225239	0	

already at $F = 0.06$ a.u. the situation has changed and the in-field potential curve supports less bound vibrational states than the field-free curve. This trend continues, and at $F = 0.12$ a.u. only one bound vibrational state is left. As was discussed in Sec. II this fully adiabatic limit describes the situation where the variation (e. g. the turn on) of the field is so slow that both, electrons and nuclei can adiabatically follow the changing field.

Depending on the pulse duration and the photon frequency, the change of the electric-field component of a laser may be slow on the electronic time scale, but fast on the nuclear one. In this frozen-nuclei limit bond softening can occur, since the unchanged field-free nuclear wave packet moves on the adiabatic potential curve that has a lowered potential barrier. In fact, the whole potential curve moves to lower energies. In Table I the index $v_{\text{max,froz}}$ of the highest-lying bound vibrational state is given for the frozen-nuclei case in which there is of course a continuous decrease of the number of bound states, since both the Stark shift of the potential well and the suppression of the barrier due to the avoided crossing support bond softening. Already at $F = 0.10$ a.u. even the lowest vibrational level becomes unbound. In the limit of nonmoving nuclei, i.e., if the field intensity does not only reach its maximum value fast on the time scale of nuclear motion, but remains at that strength only for a time that is too short for the nuclei to move, no bond softening will occur at all. It should be noted that in this work the determination of the highest vibrational bound states has been performed ignoring possible tunneling of the nuclei. Thus a vibrational state is supposed to be unbound, if its energy lies above the energy of the corresponding potential barrier. Finally, it may be noted that the question to which extent bond softening, i.e., field-induced dissociation due to the change of the potential barrier, really occurs in a certain experiment depends of course also on the probability for the nuclei to pass over the barrier, while it is suppressed. This question can only be answered by a detailed wave-packet study.

B. Enhanced ionization

Besides dissociation, the molecular ions created from tunnel ionization during the rise of the laser-pulse intensity may be further ionized. At some degree of ionization, the electronic ground-state potential curve of the multiplely charged ion may be repulsive and the ion will dissociate. A good example is molecular hydrogen, where the doubly ionized system can evidently not support any vibrational bound state and describes the repulsive interaction of two protons. This ionization-induced dissociation in laser fields is termed Coulomb explosion. The experimental investigation of Coulomb explosion due to laser-molecule interactions yielded, however, a surprising result. The observed kinetic-energy distribution of the dissociation fragments turned out to be surprisingly narrow (see e.g. Ref. [36] and references therein). One possible explanation would be that the ionization rate of the precursor state to Coulomb explosion (H_2^+ in the case of Coulomb explosion of H_2) possesses an R-dependent ionization rate that is strongly peaked at a specific (comparatively large) internuclear distance. This explanation was supported first by semiclassical models [37,38], then by quantum-mechanical calculations for H_2^+ [7,8]. Although the semiclassical explanation provides a very simple and intuitive picture, one should be aware that it does not explain the phenomenon completely [8].

Based on the quantum-mechanical calculation it is clear that enhanced ionization occurs in fact due to a field-induced avoided crossing between two potential curves [7,8]. It is, however, not the potential curve of the lower state that shows an avoided crossing, but the upper one. This is understandable, since the upper curve bends sharply upwards, and may then cross higher-lying states that are not so strongly affected by the field. As a consequence, the observation of enhanced ionization requires a nonzero population of the upper state. If the external field is turned on in an adiabatically slow way, all population would be in the lower state, and thus no enhanced ionization is observable. Since the electric field induced by a linearly polarized laser is not static, but varying with time, a sufficiently high frequency of the laser compared to the velocity of the nuclei can induce nonadiabatic transitions, and thus population of the upper state, leading finally to enhanced ionization. It should be noted, however, that already the finite velocity of the nuclei may be sufficient to induce nonadiabaticity into the process. Consider a vibrational state of the molecular ion that is populated by tunnel ionization of the parent neutral molecule and becomes dissociative due to field-induced bond softening. While the nuclei pass over the suppressed barrier, they pass a regime where the two potential curves (lower and upper electronic state of the ion) are strongly coupled. Only if the nuclei move sufficiently slowly over the barrier, the ion will remain on the lower potential curve. For any finite velocity, there is, however, a certain probability (that may be estimated e. g. by the Landau-Zener formula) that the ion will change to the upper state. In this case, enhanced ionization could even occur in the limit of a static electric field.

Considering neutral molecules like H_2, it was concluded that similarly to bond softening there should be no enhanced ionization, since the potential curve of the first excited (singlet) state should (due to the missing coupling with the ground state) not be strongly influenced by the field. Nevertheless, in Ref. [14] numerical evidence was found for enhanced ionization in neutral H_2 when performing a time-

TABLE II. Coefficients $\tilde{c}_{1,k}^{\theta,F}$ [as defined in Eq. (5)] for the adiabatic ground state of H_2 in a field with strength $F=0.08$ a.u. The index k denotes the index of the adiabatic field-free state of ${}^1\Sigma$ symmetry.

R (units of a_0)	$k=1$	$k=2$	$k=3$	$k=4$	$k=5$
1.40	0.972432	−0.185075	0.036629	0.086485	0.000614
2.00	0.924696	−0.310491	0.082070	0.075933	0.105005
3.00	0.781653	−0.403367	0.102341	0.075653	0.092708
4.00	0.596661	−0.473920	0.322228	−0.075664	0.136885
5.00	0.229922	−0.287121	0.348006	−0.094713	−0.103692
6.00	−0.114035	−0.055541	0.569513	−0.125108	−0.037765
8.00	−0.003198	−0.016422	0.450827	−0.014550	0.056668

dependent quantum-mechanical study of a one-dimensional model H_2 molecule. The seen effect was explained in terms of the dipole coupling between the ground and the first excited (singlet) state ($B^1\Sigma_u$). This coupling peaks around a certain range of R, though it remains finite even in the limit of $R\to\infty$. Noteworthy, two maxima were found in the one-dimensional numerical simulation.

In Fig. 1(b) the ionization rates (proportional to the imaginary part of the energy) of the two lowest potential curves are shown. The avoided crossing in the real energy plane corresponds now to a true crossing in the imaginary plane. In the intermediate R range, close to the field-induced (avoided) crossing, the ionization rate is rather different from the one expected from the R dependence of the vertical ionization potential. The reason is that in this R regime both potential curves are strongly coupled and thus both states comprise a mixture of the corresponding field-free states. When a molecule starting to dissociate from the covalent ground state enters the region of the (avoided) crossing, it will gain an admixture of the upper ionic state. Since the ionic component has a much larger ionization probability (the electron in H^- is only very weakly bound), the ionization rate is dominated by the ionic component in the wave function. Beyond the (avoided) crossing, the molecule may regain its covalent character (diabatic limit) and thus a lower ionization rate (converging for $R\to\infty$ to that of two neutral H atoms) or it may dissociate into ionic fragments (adiabatic limit) and thus finally adopt the large ionization rate of H^-. The former case results in an enhanced-ionization pattern as is known from e.g. ${H_2}^+$ and shows a sharp peak in the ionization rate for a narrow R range. In the adiabatic limit the ionization rate will drastically increase in the small R range close to the (avoided) crossing, but it will not diminish afterwards. However, the adiabatic limit implies slow velocities, and in this case the relatively sharp increase of the ionization probability within a relatively short R range may be sufficient to detect almost only protons stemming from this R range. Also this could therefore explain a comparatively narrow kinetic-energy distribution.

As is apparent from the present discussion both effects, bond softening and enhanced ionization, occur in H_2, and they are both caused by the same quantum-mechanical phenomenon, the occurrence of a field-induced (avoided) crossing between potential curves. From the analysis of the results and also by comparing the $R\to\infty$ limit of the adiabatic ground-state potential curve [9], a natural explanation of this effect is based on the behavior of some high-lying ionic state in an external electric field. In order to support this interpretation even further, it is of interest to identify the excited state shown in Fig. 1(a) in more detail. For this purpose the in-field states have been calculated in terms of the field-free eigenstates [cf. Eq. (5)]. The coefficients $\tilde{c}_{1,k}^{\theta,F}$ of the adiabatic ground state are presented in Table II for $F=0.08$ a.u. as a function of the internuclear distance R. For small values of R the ground state in the field is clearly dominated by the field-free ground-state wave function. With increasing R this contribution decreases steadily, and at $R=8.0a_0$ there is practically no contribution left from the field-free ground state. This confirms again that the adiabatic in-field state does not dissociate into two neutral ground-state H atoms. The decrease of the contribution of the field-free ground state is, up to the field-induced avoided crossing at $R\approx 4.0\ a_0$, accompanied by a steady increase of the contributions of the field-free second and third ${}^1\Sigma$ states, $B^1\Sigma_u^+$ and $E,F^1\Sigma_g^+$. While the strong admixture of $B^1\Sigma_u^+$ appears to be natural in view of the large dipole moment between the field-free ground ($X^1\Sigma_u^+$) and excited state $B^1\Sigma_u^+$, the admixture of $E,F^1\Sigma_g^+$ is not immediately intuitive, since the dipole moment between $X^1\Sigma_u^+$ and $E,F^1\Sigma_g^+$ vanishes for symmetry reasons. The large values of $\tilde{c}_{1,3}^{\theta,F}$ indicate a strong indirect coupling via the $B^1\Sigma_u^+$ state. Beyond the avoided crossing, the contribution of $B^1\Sigma_u^+$ decreases, while that of $E,F^1\Sigma_g^+$ increases until $R\approx 6.0\ a_0$ is reached. Then the latter contribution starts to decrease slowly, but remains predominant. The fourth and fifth field-free states have to be discussed together, since in fact the fourth state is the $B'^1\Sigma_u^+$ (in the small R range up to about $3.0a_0$) and the H ${}^1\Sigma_g^+$ (afterwards), while the fifth state represents for small R values the H ${}^1\Sigma_g^+$ and for large values the B' ${}^1\Sigma_u^+$ state. For small values of R ($<2.0\ a_0$) the contribution of $H^1\Sigma_g^+$ increases strongly, but then it remains rather constant. In fact, the summed contribution of $B'^1\Sigma_u^+$ and $H^1\Sigma_g^+$ is relatively constant over the whole R range up to $6.0a_0$. As was already mentioned, all displayed contributions decrease for very large values of R.

Following the discussion given, e.g., in Ref. [39] the $B^1\Sigma_u^+$ has predominantly ionic character in the intermediate R regime ($R\leqslant 3a_0$). For larger R values it is the $E,F^1\Sigma_g^+$ that has a dominant ionic character (in its outer minimum).

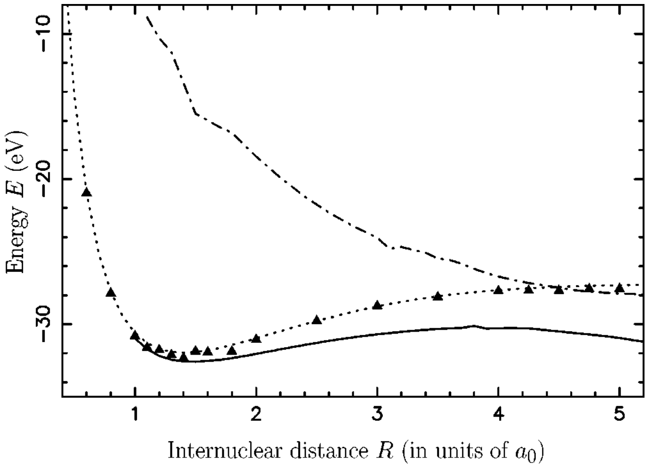

FIG. 2. Comparison of the quasidiabatic ground-state potential curve of H_2 exposed to a field of strength $F=0.08$ a.u., (triangles) with the adiabatic field-free (dotted) and in-field (solid) potential curve. Also shown is the adiabatic in-field potential curve of the first excited state (chain).

The ionic character decreases for even larger values of R due to an avoided crossing with another state. In this way the ionic character is transfered from one state to the other, as the diabatic ionic state crosses a number of states before it converges to its dissociation limit. This fact is in full agreement with the interpretation given above that it is the ionic state which is strongly coupled to the ground state, if an electric field is applied parallel to the internuclear axis. It is a shortcoming of the adiabatic description that the ground state is in fact coupled to a number of adiabatic states when R is varied, simply because the ionic character is transfered in the adiabatic picture from state to state.

C. Quasidiabatic potential curve

Another interesting analysis is based on the calculation of quasidiabatic potential curves. As was discussed before, there is no unique diabatization procedure. In the present case, the quasidiabatic ground-state potential curve of H_2 exposed to an electric field is obtained by setting the largest coupling between the field-free ground state and the other field-free states to zero. The result for $F=0.08$ a.u. is shown in Fig. 2. On the first glance a rather good agreement is found between the quasidiabatic and the field-free curve. On a second glance one notices a small shift between these two curves for large R values and around the center of the potential well. These deviations should be basically due to the Stark shift. Noteworthy, the Stark shift appears to be small at both ends of the potential well. Furthermore, the quasidiabatic curve shows an oscillatory behavior at the center of the potential well. These oscillations are also present in the adiabatic excited-state potential curve. This indicates that those latter oscillations are in fact not due to numerical inaccuracies, but due to some curve crossings. Since at those (avoided) curve crossings the states involved change their character, a diabatization procedure that ignores the predominant field-induced coupling of the ground state to the other states fails at those crossings. Consider, for example, the ground state being most strongly coupled to an excited state A. If this state undergoes an avoided crossing with another state B, both states will mix and the resulting states A' and B' are a mixture of A and B. If the ground state does not (or only weakly) couple to state B, the coupling to state A' is smaller than the one with state A. On the other hand, the coupling to state B' is larger than the one to state B. While the sum of the couplings to A and B is equal to the one to A' and B' (the adiabatic ground state curve is smooth), this is not the case, if the coupling to one state (A or A') is set to zero as is done in the used diabatization procedure.

The diabatization procedure has thus revealed further field-induced curve crossings and shown a large similarity between the quasidiabatic and the field-free ground-state potential curves. However, in its present implementation (and due to the field-induced curve crossings that occur for the state to which the ground state is coupled most strongly) the diabatization procedure does not result in a smooth curve. Therefore, it cannot be used to obtain the nuclear wave function within the quasidiabatic limit. However, considering the close agreement with the field-free curve, the latter may be used for an approximate determination of the nuclear wave function. Note, the Stark shift appears not to be linear (as a function of R), and thus the resulting nuclear wave function is certainly only an approximation to the correct diabatic one.

In the context of the diabatization procedure it is also interesting to analyze the question which of the states is most strongly coupled to the ground state. It turns out that in the whole R range up to 8 a.u. (except for $R<1.0\,a_0$) the coupling to the first excited electronic state ($B^1\Sigma_u$) is predominant. In other words, in that R range the dipole coupling of the field-free ground state to the ($B^1\Sigma_u$) is largest. Considering this finding together with the analysis of the in-field states in the field-free basis given above and the found quasidiabatic potential curve it is clear that the admixture of the different field-free states occurs in the whole R range discussed via the $B^1\Sigma_u$ state. As a check of the accuracy of the present calculation, it is interesting to note that the coupling matrix element between $X^1\Sigma_g^+$ and $B^1\Sigma_u$ agrees (for $\theta=0$ and the different basis sets) with the very accurate dipole matrix elements reported in Ref. [40] within 10%, in the range up to 5 a.u. even within 1%.

D. Comparison between $H_2{}^+$ and H_2

In comparison to bond softening and enhanced ionization found in molecular cations with odd electron number, especially $H_2{}^+$, it is important to emphasize the following aspects. In the ionic case, bond softening is induced by the diverging dipole moment between the field-free ground and first excited state for $R\rightarrow\infty$. As a consequence of the field, the two states repel each other, tending to $\pm\infty$ for $R\rightarrow\infty$. The lower potential curve bends downwards and thus the potential well becomes shallower (and disappears for sufficiently large field strengths), allowing for bond softening. Since the upper curve bends upwards, a new potential well appears (in the adiabatic limit) that leads to bond hardening.

The internuclear distance at which the field-induced avoided crossing occurs is rather independent of the field strength.

In the case of a covalent molecule (like H_2) the field-free ionic states (in the case of H_2 there are only two since H^- has only one bound state) are strongly affected by the electric field, because they behave like a dipole. The ionic state corresponding to a dipole parallel to the field bends downwards. It creates an avoided crossing with the ground state, since the position of the latter is nearly unaffected by the field. The position of the avoided crossing (and its coupling strength) depends rather strongly on the field strength. The adiabatic in-field ground state changes character at the crossing and continues along the ionic state after the crossing. As a consequence, bond softening occurs, but the effect is weaker than in ${H_2}^+$, i.e., stronger fields are required. However, in contrast to ${H_2}^+$ and comparable systems no bond hardening occurs for H_2, since the upper adiabatic in-field state remains purely dissociative.

In the case of ${H_2}^+$ no enhanced ionization occurs for the adiabatic in-field ground state, since the potential curve bends downwards and is thus not crossed by any excited state [7,8]. The upper curve that bends upwards due to the field-induced coupling with the ground state crosses higher-lying field-free states that are less affected by the electric field or even bend downwards. At those avoided crossings the adiabatic in-field upper state changes character and due to the admixture of the higher-lying field-free state (with smaller ionization potential) the ionization rate increases rapidly in the crossing region, leading to enhanced ionization. For enhanced ionization to be observable, it is required to populate the upper in-field state which in practice may arise from nonadiabatic transitions or from the fast oscillation of the electric field of the laser.

In the case of H_2 (and correspondingly also for other covalent molecules), the field-induced avoided crossing of the ground state with the ionic state leads to enhanced ionization of the adiabatic ground state (in contrast to the case of H_2^+ and other diatomic molecular ions with an odd number of electrons). Thus no population of the excited state is needed for this effect.

The experimental observation of bond softening in ${H_2}^+$ requires either a study of highly lying rovibrational states or sufficiently strong electric fields (or electric field components). The same is true for H_2, but in this case bond softening is weaker and thus requires stronger fields. At the same time the ionization rate of H_2 is larger and thus bond softening is more difficult to observe in H_2 than in ${H_2}^+$. The best possibility is either the study of highly lying rovibrational states or to consider a different type of molecule. The observation of enhanced ionization in ${H_2}^+$ (and similar systems) requires population in the upper electronic in-field state and the ion to reach the critical distance. In practice, it seems that this happens, since the ion is created at the rising edge of the laser pulse from H_2 which also populates dissociative rovibrational states of ${H_2}^+$. Another possibility is the field-induced bond softening that can direct the ion to the critical distance for enhanced ionization. Population of the upper electronic state can then be induced through nonadiabaticity, either due to the laser frequency or due to nuclear motion.

Owing to the unfavorable ratio of ionization and bond-softening induced dissociation, H_2 will usually ionize before the critical distance is reached, except if it was prepared in a highly lying rovibrational state. However, no electronic excitation is required for observing enhanced ionization, but the nuclear motion (or the laser frequency) has to be sufficiently fast, if a distinct peak instead of a sharp rise should occur in the ionization rate.

E. Simplified numerical models

It is worthwhile to discuss the possibility to numerically treat bond softening and enhanced ionization for larger systems, such as many-electron diatomic or even polyatomic molecules, since the present results obtained for H_2 clearly imply that similar effects should be present in any (covalent) neutral molecule. As was discussed in Sec. II standard quantum-chemistry codes often provide the option to perform finite-field calculations, and the calculation of the necessary matrix elements does not pose any additional difficulty. The present work offers the unique possibility to discuss at least in the case of H_2 the reliability of such finite-field calculations for strong fields, since it is possible to directly compare the approximate results with the (within the given basis set) accurate results obtained using the complex-scaling method. In this context it should also be mentioned that in a recent theoretical study a standard quantum-chemistry code has been used to investigate the related problem of electric-field effects on the ionic-neutral curve crossing in alkali halides [41]. In the case of an alkali halide (ionic ground state), there exists an avoided crossing with the first excited state (covalent character) already in the field-free case. As the ionic state is energetically favorable in the field (see above), its bending down in the field can finally lead to the disappearance of the avoided crossing, if the field is sufficiently strong. This is the opposite situation compared to the one that is considered in the present work.

In order to evaluate ionization rates on the *ab initio* level there is the evident problem that standard $\mathcal{L}^2$-type basis functions will only yield real energy values, and thus not the width. Possible extensions would be to add a complex absorbing potential, but this will result in a complex eigenvalue problem that definitely has to be solved separately from the standard quantum-chemistry code. Another possible approach would be to perform a (real) variation of the basis functions and an investigation of the real-scaling trajectories. Stable regions should indicate a resonant state, and in principle, it is even possible to extract the width of the state from such trajectories (see e.g., Ref. [42] and references therein). It has to be emphasized, however, that with increasing field strength (and depending on the basis set) more and more continuum states will appear *below* the ground state, and thus standard quantum-chemistry codes which often obtain the lowest-lying eigenvalues by a variational procedure will run into difficulties to provide a sufficient number of (converged) states in order to reveal the ground state.

With respect to bond softening the situation may be more favorable, at least if only approximate potential curves are seeked for. In this case it may be possible to concentrate on

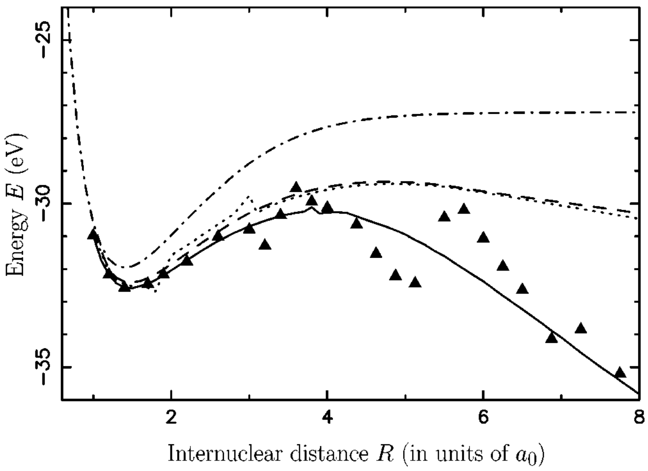

FIG. 3. Adiabatic potential curves of H_2 exposed to a field of strength $F = 0.08$ a.u. Shown is the ground-state obtained using the complex-scaling method (solid) and a complex-scaling angle $\theta = 0$ corresponding to a standard finite-field calculation (triangles). Also shown are the results using $\theta = 0$ and only the three (dashed) or five (dotted) lowest-lying field-free adiabatic states in the calculation. For comparison, the field-free ground-state potential curve is also given (chain).

a small number of states whose coupling to the ground state has to be evaluated. The in-field potential curves are then obtained from the diagonalization of the resulting (dimensionally reduced) Hamiltonian. As is typical for such essential-state analyzes, it is of course important to identify the relevant electronic states in a specific system. The present results suggest that in the case of a covalent ground state, it is important to include the states with ionic character, especially those having an ionic dissociation limit. In contrast to the case of H_2 where only one bound state of H^- exists one has probably to consider more than one state when treating other molecular systems. A practical problem can be the fact that also in other molecules there is not one adiabatic ionic state, but due to (avoided) crossings with a series of states the ionic character is R-dependently distributed over a number of states. In this case it may be more useful to try to simulate the diabatic ionic state (from its ionic components) and to calculate the interaction of this diabatic ionic state with the ground state. This procedure should work especially well, if the field-induced crossings occur for large R values where a diatomic molecule behaves anyhow more like two interacting atoms.

An expansion in field-free adiabatic states appears on the other hand not very likely to work out, if the analysis of the adiabatic ground-state wave function exposed to a field of strength $F = 0.08$ a.u. given in Table II is considered. While for small values of R the (square of the) coefficients of the lowest 3–5 adiabatic field-free states almost add to 1, this is not the case for large values of R. In fact, performing a calculation including only the lowest-lying 2–8 adiabatic field-free states in the calculation gives a reasonable in-field adiabatic potential curve for R values below $R \approx 2.5 a_0$, but increasingly deviates from the result of the full calculation with increasing R. In Fig. 3 the results using the lowest-lying 3 or 5 field-free states are shown. The Stark shift around the center of the potential well is rather well reproduced, especially when considering the small number of states involved in the calculation. Even the effect of bond softening is predicted in this simplified calculation. However, due to the increasing difference between the correct and the approximate results with increasing R, a quantitative result cannot be obtained. In addition, the behavior of the approximate potential curves for large R values differs substantially from the slope predicted by the dipole H^+H^- that in fact is the origin of the bond softening, as was discussed above. It is also interesting to note that the agreement between the three- and the five-state model is rather good, especially in the large R part. This indicates the difficulty to improve on this model and the danger of erroneously assuming convergence. Even more problematic is the fact that the five-state model shows spurious oscillations at the outer part of the potential well, indicating that in the five-state model an important coupling between states is left out. In other words, if one attempts such an essential-state analysis, one has to be careful to include complete sets of interacting states.

Alternatively to the essential-state analysis, it is of course also possible to use the results obtained from diagonalizing the in-field Hamiltonian in some finite basis set which corresponds to the standard finite-field approach already mentioned. In the present case, this corresponds to a calculation where the complex-scaling angle is fixed to zero. In Fig. 3 the adiabatic ground-state potential curve obtained with one of the basis sets is compared to the complex-scaling result. Clearly, the results obtained on the real axis show rather pronounced oscillations. The result obtained for $R < 3.0 a_0$ is, however, in very good agreement with the potential curve obtained from complex scaling. This is to be expected from the essential-state analysis where also good agreement was found in the small R regime, because the full finite-field calculation should not be worse than the essential-state approach (except for accidental error compensation). However, rather strong oscillations occur for larger values of R, and they are most pronounced in the R interval $(4.5–6.5)a_0$, while the amplitude decreases for even larger R values. In general, the real curve oscillates around the complex-scaling result, and if the curve were freed from the oscillations (by some smoothing procedure), a reasonable approximation to the complex-scaling result may be obtained. The basis set selected for the graph uses R-independent basis-set parameters in order to clarify that all oscillations are only due to the shortcoming of the real-axis calculation, and not perhaps due to an R-dependent change in the basis set. Nevertheless, it is clear from Fig. 3 that without the knowledge of the correct result, it would be very difficult to know how one would have to interpret the finite-field calculation, and whether the oscillations are physical or not.

The source of the oscillations is the coupling of the resonant state with the underlying (discretized) continuum states. This explains also the absence of the oscillations in the three-state model. In that case no continuum states are included in the calculation and therefore the ground state cannot adopt any width. From the complex-scaling trajectories it is clear that a resonant trajectory can start on the real axis at some rather distant point. As an empirical rule of thumb one can say that the change of the energy position of the resonant root in between $\theta=0$ and $\theta_{\rm opt}$ at which the resonant trajectory is most stable is comparable to the width of the state. This explains that one should expect rather small oscillations, and in fact rather small deviations of the position from its correct value, if the ionization probability is small. This is in agreement with the very good results obtained on the real axis for small R values, since there the ionization rate is very small. However, from this rule alone one would expect that the amplitude of the oscillations should continuously increase for increasing R, since the ionization width increases continuously (in the adiabatic limit discussed here). Analyzing the complex trajectories in more detail, it turns out that the reason for the very strong oscillations is directly due to the avoided crossing. The trajectories of the two strongly interacting states show a strong influence on each other and change simultaneously as a function of R. Thus it appears as strong oscillations will more or less necessarily occur if an avoided crossing is present. Similar oscillations, though with an erratic phase and slightly different amplitudes are observed with all basis sets employed. In the case of R-dependent basis sets the structure becomes even more erratic, and thus no clear oscillations but strong fluctuations occur.

There exists an additional problem with the finite-field (real-axis) calculation. With increasing field strength, but also for increasing values of R there are, as already mentioned, more and more (discretized) continuum states appearing below the adiabatic ground state. This is not only a numerical problem if adopting a standard quantum-chemistry code that often determines only the lowest eigenstates (using an iterative scheme), but also a practical one. How is the correct state identified? Using the present complex-scaling approach, this is simplified, since the continuum states show a much more pronounced θ dependence than metastable states like the field-free bound states. The curve in Fig. 3 was obtained by simply identifying the resonant trajectory, and selecting its starting value on the real axis. If a complex-scaling calculation cannot be done, one has to adopt a different identification scheme. One way would be to analyze the wave function and to follow the root with the largest overlap to the previous R value. However, this approach will not solve the problem of the oscillations, and it will yield quasidiabatic curves, since in the case of a possible avoided curve crossing (as it occurs in the present case) the overlap will be the largest for the diabatic continuation beyond the crossing. The most similar approach to complex scaling (or adding a complex absorbing potential) consists in performing real scaling, and thus adopting the already mentioned stabilization method (Ref. [42] and references therein). Instead of scaling the Hamiltonian, it is often easier to scale (inversely) the basis functions. The underlying concept of (real) stabilization theory has been discussed (for field-free resonances) before. Avoided crossings should become evident, and even the problem of the spurious oscillations may be cured. Experience shows, however, that a very accurate determination of the resonance position (or even its width) by the real stabilization method is usually difficult and demands better basis-set quality than the complex-scaling method.

IV. CONCLUSION AND OUTLOOK

The behavior of H_2 molecules exposed to a strong static electric field has been studied. On the basis of the quasistatic approximation this allows also the prediction of the behavior of H_2 exposed to an ac or low-frequency laser. For this purpose, a three-dimensional, fully correlated *ab initio* method has been developed and described that is, however, presently limited to the case of a parallel orientation of the internuclear axis and the external field. This should be realistic, if the external field leads to a corresponding alignment of the molecules, as was predicted to happen at least in the case of light molecules. The present work allows to predict quantitatively *ab initio* ionization rates for H_2 exposed to a strong electric field.

Based on the present calculation two molecular strong-field phenomena, bond softening and enhanced ionization, are predicted to occur for H_2, although the lack of existence of bond softening had been predicted about 40 years ago. It is shown that both effects have the same origin, the occurrence of an (avoided) crossing between the covalent ground state and the ionic excited state. Based on this interpretation, the existence of both phenomena is predicted to occur in any covalently bound neutral molecule. The similarities and differences to the case of diatomic molecular ions with an odd number of electrons, especially $H_2{}^+$, is explained. The important role of (a)diabaticity (due to nuclear motion and or the change of the external field) is discussed in the form of the multiphoton, sudden turn-on, fully adiabatic, vibrationally diabatic, frozen-, and non-moving-nuclei solutions. The possibility to qualitatively or quantitatively predict bond softening and enhanced ionization for more complicated systems than H_2 is discussed by comparing the results obtained for H_2 using the full numerical approach and simplified alternative methods. Although there are evident numerical difficulties, the results are still rather encouraging, especially with respect to predicting bond softening.

The present work indicates the directions of the most important future steps of investigation for which the present study has paved the path. First, a calculation of the orientational dependence of the ionization rate of H_2 is very timely. Second, the time dependence of nuclear motion and (or) the external ac or low-frequency laser field should explicitly be included in the study. Work along these lines is currently in progress.

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