

Superdressed H_2^+ and H_3^{2+} molecular ions in intense, high-frequency laser fields

T. Zuo and A. D. Bandrauk

Laboratoire de Chimie Théorique, Faculté des Sciences, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

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We study the radiative distortion of the lowest two potential surfaces of H_2^+ and H_3^{2+} molecular ions in a superintense ($I > 10^{16}$ W/cm²), high-frequency, linearly polarized laser field, using the space-translation or acceleration representation of laser-matter interaction. The electron clouds undergo field-induced redistribution in the molecular ions due to the presence of field-induced “dichotomous” dressed Coulomb potentials. Such super-field-dressed systems have a greater tendency to transfer electronic charge into the region between the nuclei and hence become more “stable” than the field-free ones. For example, at the equilibrium nuclear separation the dissociation energy of the superdressed H_2^+ is found to increase by about 20% compared with the field-free H_2^+ . More dramatically, the lowest two surfaces of H_3^{2+} that are repulsive in zero field become attractive (bonding) in the presence of an intense, high-frequency field. The possibility of molecules becoming stabilized against both ionization and dissociation in superintense fields is discussed.

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Atoms and molecules are expected to undergo considerable distortion when exposed to a superintense field, i.e., intensity greater than $I_0 = 3.5 \times 10^{16}$ W/cm², the atomic unit of field intensity [1]. A good example has been the case of hydrogen in high-intensity, high-frequency laser fields, studied by several groups. Among them, Su *et al.* [2] have carried out numerical experiments using a one-dimensional hydrogen atom and found the ionization rate decreasing when the laser intensity increased beyond I_0 . This ionization suppression was later confirmed numerically by Kulander *et al.* [3] for a realistic three-dimensional hydrogen atom. The space-translation or acceleration [also known as the Kramers-Henneberger (KH) or Bloch-Nordsieck [1]] representation was found useful to interpret the results. In fact, the radiative distortion of the hydrogen atom at the high-intensity, high-frequency limit has been thoroughly investigated by Gavrilin and co-workers in the space-translation frame [4]. Applications of the quantum version of this representation to molecular systems can be found in the work of Nguyen-Dang and Bandrauk [5–8], where it was shown that electronic potentials will be severely distorted.

In this work, we consider H_2^+ and H_3^{2+} in superintense, linearly polarized, high-frequency fields. In the space-translation representation, the single electron is subject to the relative Coulomb field of quickly oscillating nuclei, with the oscillation amplitude and frequency dictated by the applied laser field. A first-order treatment of the above system is naturally the replacement of the oscillatory Coulomb potential by its time-averaged values for high frequencies, hereafter referred to as the superdressed potential. Since an oscillating nucleus spends a longer time in the vicinity of two new field-induced turning points $\alpha_0 = E_0/\omega^2$, the time averaging dichotomizes the Coulomb potential with singularities at these two turning points. The time-average scheme is justified if the laser frequency is very high. Higher-order corrections have been discussed by Gavrilin [4] for the hydrogen atom. Assuming the first order to be dominant, we see that all the radiative dressing is now embedded in the superdressed potential which depends on laser conditions and molecular internuclear distances. The Schrödinger equation of a single

molecular electron in this superdressed potential can be solved numerically without difficulty if the Born-Oppenheimer approximation is applied as originally developed by Nguyen-Dang and Bandrauk [5–8]. The field-induced renormalization of the adiabatic electronic potential can then be compared to the field-free potential and exhibits new structure leading to stabilization.

We have studied the lowest two superdressed potential surfaces of H_2^+ and H_3^{2+} . We have found that the laser dressing enhances the binding of the molecules ions. We shall see that this is due to the ability of these dressed molecules to transfer a great amount of electronic cloud into the region between the nuclei—a consequence of the replacement of the Coulomb potential by the dichotomous dressed potential for electrons with no change in the interaction between nuclei in the dipole approximation [5–8]. A significant case is where the unstable H_3^{2+} is found to be stable due to this high-field dressing.

The dressed potential surfaces of H_2^+ . In the Born-Oppenheimer approximation, the time-dependent Schrödinger equation of H_2^+ interacting with a laser field linearly polarized along the internuclear axis (the z axis) is given by (in atomic units)

$$i \frac{\partial}{\partial t} \Psi(R, \vec{r}, t) = \left(\frac{1}{2} \vec{p}^2 + V(R, \vec{r} + \vec{\alpha}(t)) \right) \Psi(R, \vec{r}, t), \quad (1)$$

where we have used the space-translation representation of the laser-matter interaction (see, e.g., [5,9]) and $\vec{\alpha}(t) = (E_0 \hat{z} / \omega^2) \cos(\omega t)$, with E_0 and ω being the electric field amplitude and laser frequency, respectively, and \hat{z} a unit vector. In Eq. (1), the ponderomotive energy $A^2(t)/2c^2$ has been neglected as it shifts all surfaces equally [1]. For H_2^+ the field-free Coulomb potential is given by

$$V(R, \vec{r}) = - \frac{1}{|\vec{r} - \hat{z}R/2|} - \frac{1}{|\vec{r} + \hat{z}R/2|}. \quad (2)$$

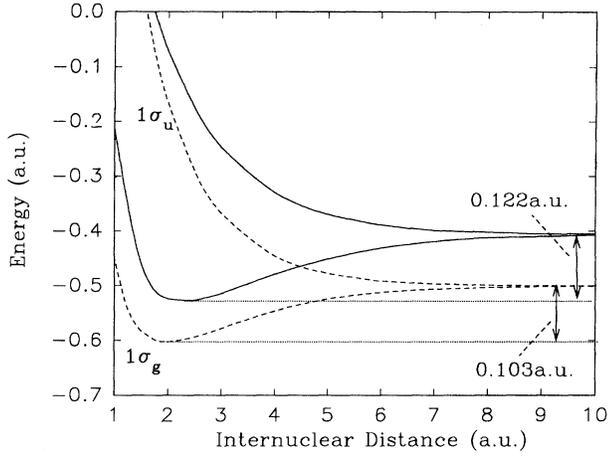


FIG. 1. The lowest two potential surfaces of H_2^+ . Solid lines: surfaces dressed by a field giving $\alpha_0=1$ a.u.; dashed lines: field-free surfaces.

In the presence of the field, the dressed potential $V(R, \vec{r} + \vec{\alpha}(t))$ is periodic in time, so a Fourier expansion or Floquet analysis gives

$$\Psi(R, \vec{r}, t) = e^{-iEt} \sum_{n=-\infty}^{\infty} e^{-in\omega t} \Psi_n(R, \vec{r}) \quad (3)$$

and

$$V(R, \vec{r} + \vec{\alpha}(t)) = \sum_{n=-\infty}^{\infty} e^{-in\omega t} V_n(R, \vec{r}). \quad (4)$$

Substituting Eqs. (3) and (4) into (1) and keeping only the first-order static term ($n=0$), one has

$$[\frac{1}{2}\vec{p}^2 + V_0(R, \vec{r})]\Psi_0(R, \vec{r}) = E(R)\Psi_0(R, \vec{r}), \quad (5)$$

where the space-translation potential is defined as

$$\begin{aligned} V_0(R, \vec{r}) &= \frac{1}{2\pi} \int_{-\pi}^{\pi} V(R, \vec{r} + \vec{\alpha}(t)) d(\omega t) \\ &= -\frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{1}{|\vec{r} + \vec{\alpha}(t) - \hat{z}R/2|} d(\omega t) \\ &\quad - \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{1}{|\vec{r} + \vec{\alpha}(t) + \hat{z}R/2|} d(\omega t) \\ &= V_{0c}(\vec{r} - \hat{z}R/2) + V_{0c}(\vec{r} + \hat{z}R/2). \end{aligned} \quad (6)$$

In Eq. (6) following [10] we have defined V_{0c} as

$$\begin{aligned} V_{0c}(\vec{r}) &= -\frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{1}{|\vec{r} + \vec{\alpha}(t)|} d(\omega t) \\ &= -\frac{2}{\pi} \frac{1}{\sqrt{r_+ r_-}} K(\sqrt{(1 - \hat{r}_+ \hat{r}_-)/2}), \end{aligned} \quad (7)$$

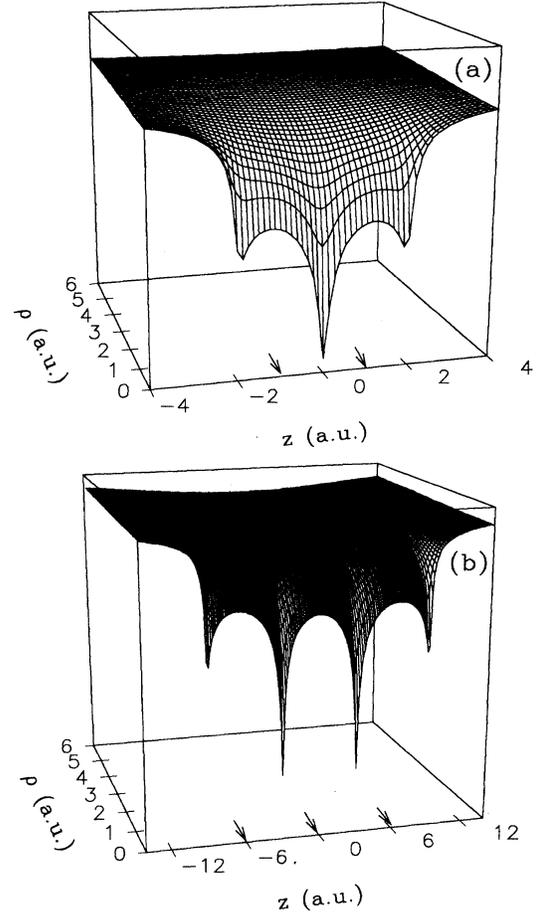


FIG. 2. The superdressed potentials in the cylindrical (ρ - z - θ) coordinate (the potential is symmetric in θ). The position of the nuclei are marked with arrows. (a) H_2^+ at internuclear separation $R=2$ a.u., $\alpha_0=1$ a.u.; (b) H_3^{2+} at a distance between two outer nuclei $R=12$ a.u., $\alpha_0=3$ a.u.

where $\vec{r}_{\pm} = \vec{r} \pm \alpha_0 \hat{z}$, $\alpha_0 = E_0/\omega^2$, and K is the complete elliptic integral of the first kind. The lowest two potential electronic surfaces [including the Coulomb repulsion between nuclei, $E(R) + 1/R$] governed by Eq. (5) for $\alpha_0 = E_0/\omega^2 = 1$ a.u. are plotted in Fig. 1 as solid lines and are to be compared with the field-free (dashed lines) $1\sigma_g$ and $1\sigma_u$ surfaces. These were obtained numerically from the Feit-Fleck spectral method which gives the electronic energies $E(R)$ and the electronic wave functions [11]. It is seen that, while the dressed surfaces are shifted upwards because of field-induced polarizations (dressings), the dissociation energy increases from 0.103 a.u. (2.80 eV) to 0.122 a.u. (3.32 eV). The separated-atom (large- R) limit for the dressed H_2^+ goes to the dressed hydrogen atom energy. At $R=10$ a.u. this energy is 0.406 a.u., in very good agreement with the calculation by Pont *et al.* [12]. The increase of the dissociation energy can be understood in the following way. It is known that the space-translated or superdressed Coulomb potential $V_{0c}(\vec{r})$ has two $r^{-1/2}$ singularities along the laser polarization direction, at $\pm \alpha_0 \hat{z}$, instead of a single Coulomb minimum. We shall see that the essential physics are gov-

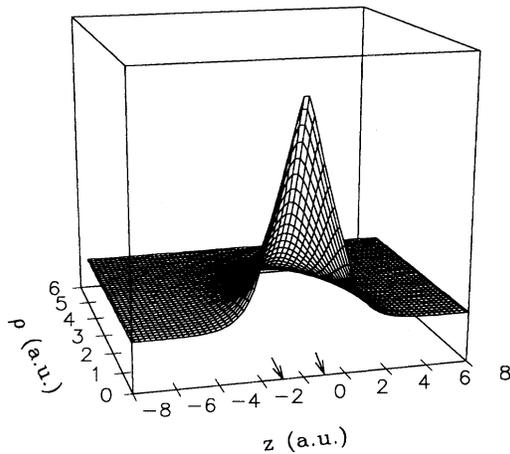


FIG. 3. Same as Fig. 2(a) but for the ground-state wave functions.

erned primarily by the potential “dichotomy.” In the case of H_2^+ , the superdressed potential [Eq. (6)] generally has four minima, at z values $-R/2 - \alpha_0$, $-R/2 + \alpha_0$, $R/2 - \alpha_0$, and $R/2 + \alpha_0$, respectively. Clearly for a given laser condition, e.g., $\alpha_0=1$ a.u., the dressed potential becomes a triple-minimum potential when $R/2 = \alpha_0$ ($R=2$ a.u.) with the middle minimum twice as attractive as the two external ones [see Fig. 2(a)]. Obviously the ground state supported by such a triple-minimum potential has most of its electronic cloud centered at the origin, as shown in Fig. 3. Since the two positively charged nuclei are originally at position $z = \pm R/2$, it is readily anticipated from the well-known electrostatic theorem of chemical bond theory (see, e.g., [13]) that the above superdressed system will tend to bind together more strongly than its field-free counterpart where the electronic cloud is centered at the two nuclei. The condition $R/2 = \alpha_0$, however, should be only regarded as a guideline to the potential surface minimum (the dressed molecular equilibrium separation). The exact position of this minimum is exclusively determined by the quantum-mechanical solution of Eq. (5) in the neighborhood of $R = 2\alpha_0$.

The dressed potential surfaces of H_3^{2+} . Under the same assumption as for H_2^+ in the last paragraph, we consider the linear H_3^{2+} molecular ion. Without external field, linear H_3^{2+} is unstable against dissociation, namely, the ground-state potential surface is always repulsive, as discussed by Rosenthal and Wilson [14]. In analogy to H_2^+ , the superdressed potential for H_3^{2+} is now given by the three-center expression,

$$V_0(R, \vec{r}) = V_{0c}(\vec{r} + \hat{z}R/2) + V_{0c}(\vec{r}) + V_{0c}(\vec{r} - \hat{z}R/2), \quad (8)$$

where R is the separation between the two outer nuclei. It is seen from Eq. (8) that along the laser polarization direction we now have an attractive potential with six minima at z values $-R/2 - \alpha_0$, $-R/2 + \alpha_0$, $-\alpha_0$, α_0 , $R/2 - \alpha_0$, and $R/2 + \alpha_0$, respectively. For a given α_0 , e.g., $\alpha_0=3$ a.u. when $R/4 = \alpha_0$, this potential becomes a four-minimum potential with singularities at $-3R/4$, $-R/4$, $R/4$, and $3R/4$, respectively. The two middle minima are now twice as attractive as the two external ones [see Fig. 2(b)]. The calcu-

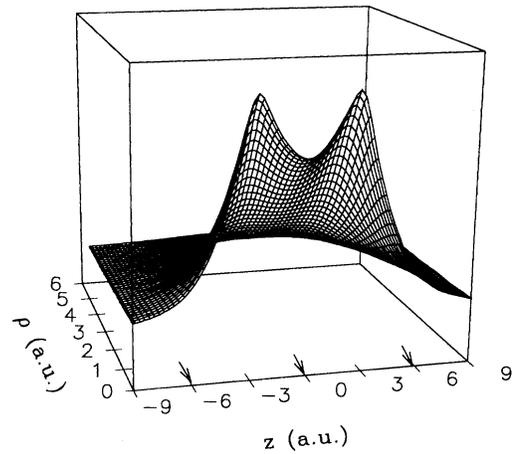


FIG. 4. Same as Fig. 2(b) but for the ground-state wave functions.

lated ground-state wave function (Fig. 4) (at the laser condition $\alpha_0=3$ a.u., $R=12$ a.u.) shows that the electronic cloud now concentrates near $z = \pm R/4$. With nuclei situated at $-R/2$, 0 , and $R/2$, this new structure of electronic clouds sandwiched between the nuclei is expected to lead to strong binding compared with the field-free situation where most of the electronic cloud is near the middle nucleus. The lowest two dressed electronic potentials as a function of the internuclei separation R , namely, the potential surfaces [including the Coulomb repulsion among nuclei, $E(R) + 1/R + 2/(R/2)$] are calculated and plotted in Fig. 5. It is seen that both surfaces are now attractive. The potential surface minima (the dressed molecular equilibrium separations) are at $R=10$ and 11 a.u. for the lower and the upper surfaces, respectively, close to the guideline condition $R/4 = 3$ a.u. It is worthwhile to note from Fig. 5 that the two surfaces go to different large R (separated-atom) limits, unlike the H_2^+ case. This is also due to the peculiarity of the three-nucleus system. At large R (with α_0 fixed and much less than R), the molecular ion's lower surface dissociates to a limit where

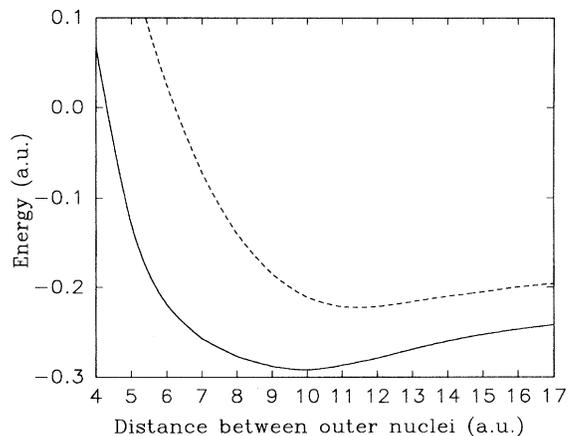


FIG. 5. The lowest two potential surfaces of H_3^{2+} dressed by field with $\alpha_0=3$ a.u. Solid line: the ground state; dashed line: the first excited state.

all of the electronic cloud stays near the middle nucleus while the upper surface dissociates to a limit where half of the electronic cloud goes to the right nucleus and half to the left nucleus. This is similar to the well known charge-transfer states in diatomic systems [15]. In the case of H_2^+ , both surfaces tend to the same large- R limit and form the charge-resonant states [15].

Discussions and conclusions. We have seen in previous sections that the space-translation method gives new super-dressed electronic potentials at high frequencies in molecules. To meet the maximum binding condition, $\alpha_0 = E_0/\omega^2$ is required to be of the same magnitude as R , i.e., a few atomic units. If we take the high laser frequency to be $\omega = 1$ a.u. (corresponding to wavelength $\lambda = 45$ nm), the condition, e.g., $\alpha_0 = 3$ a.u. leads to a laser intensity of about 10^{17} W/cm², beyond the atomic unit $I_0 = 3.5 \times 10^{16}$ W/cm².

One of the major assumptions in this work is the truncation of Eqs. (3) and (4) to first-order. This means the ionization process is entirely ignored. Although there is strong evidence from various numerical experiments on the hydrogen atom (e.g., [3]) and the H_2^+ molecular ion [16] that ionization is highly suppressed in a high-frequency, high-intensity field, a quantitative analysis of the present problem needs to include ionization. The primary purpose of this work is, nevertheless, to explore the essential physics when simple molecular systems are exposed to superintense fields. In fact, the main finding of this work, namely, an increase of the dissociation energies by the field (this is likely to result in dissociation suppression dynamically), can be correlated with the suppression of ionization. Since the ionization rate

of a molecular ion depends (increases) very sensitively on the internuclear separation R [17], less dissociation could lead to less ionization and vice versa. It will be of great interest to investigate this scenario of double suppression, i.e., suppression of both ionization and dissociation in a more complete way by solving the time-dependent Schrödinger equation for both electronic and nuclear motions. One must also include the ponderomotive energy $A^2(t)/2c^2$ in a full time-dependent treatment [18].

In summary, when dressed by superintense, linearly polarized, high-frequency laser fields, H_2^+ and H_3^{2+} form a novel quantum-chemical system where electrons are subject to “dichotomous” nuclear potentials. As a result, the field forces the electronic cloud to stay between the nuclei and hence stabilizes the molecular system against dissociation. Such nuclear stabilization was shown to occur before at the laser intensity $I < 10^{14}$ W/cm² in H_2^+ by laser-induced avoided crossings [1,19]. The stabilization observed in the present simulations is the result of high-frequency laser-induced electronic cloud reorganization within molecules.

Note added. Recently, Shertzer, Chandler, and Gavrilva [20] have reported ground-state superdressed energies of H_2^+ , i.e., the $1\sigma_g$ state only. Their result for the $1\sigma_g$ potential agrees with ours (Fig. 1).

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