New stable multiply charged negative atomic ions in linearly polarized superintense laser fields

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Singly charged negative atomic ions exist in the gas phase and are of fundamental importance in atomic and molecular physics. However, theoretical calculations and experimental results clearly exclude the existence of any stable doubly-negatively-charged atomic ion in the gas phase, only one electron can be added to a free atom in the gas phase. In this report, using the high-frequency Floquet theory, we predict that in a linear superintense laser field one can stabilize multiply charged negative atomic ions in the gas phase. We present self-consistent field calculations for the linear superintense laser fields needed to bind extra one and two electrons to form He^-, He^{2-}, and Li^{2-}, with detachment energies dependent on the laser intensity and maximal values of 1.2, 0.12, and 0.13 eV, respectively. The fields and frequencies needed for binding extra electrons are within experimental reach. This method of stabilization is general and can be used to predict stability of larger multiply charged negative atomic ions. © *2006 American Institute of Physics*.
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Singly charged negative ions in the gas phase are of fundamental importance in atomic and molecular physics and have attracted considerable experimental and theoretical attention over the past decades.[1–8] With the advancement of spectroscopic and theoretical methods, new atomic ions such as Ca^- and Sr^- with small electron affinities (about 40 meV) have been found to be stable.[9,10] However, the existence of gas-phase doubly charged atomic negative ions has remained a matter of some controversy.[6] In the sixties and seventies, there were several experiments, which claimed the detection of doubly charged atomic ions, but most of these observations have been shown to be artifacts, and no evidence of atomic dianions were observed.[11,12] Theoretically, Lieb[13] formulated an upper bound for the maximum number of electrons, N_c, that can be bound to an atomic nucleus of charge Z, $N_c \leq 2Z$. This inequality gives the first proof that H^{2-} is not stable, which is in agreement with experiments[11] and many *ab initio* studies.[3] There are many *ab initio* and density functional calculations[2] of the electron affinities. Recently,[14] we have calculated the critical nuclear charges for atoms up to $N=86$, where N is the number of electrons, the results clearly exclude the existence of any stable doubly negatively charged atomic ions in the gas phase.[14,15] However, these systems might be stable in very intense magnetic fields.[16–18]

Small dianions such as O^{2-} or CO_3^{2-} are very common in solution and solid-state chemistry, but are unstable in the gas phase.[6] Thus, there is still an open question concerning the smallest molecule that can bind two or more excess electrons with both electronic, against electron detachment, and thermodynamic, against fragmentation, stability.[19] A number of multiply-charged anions with relatively large size, more than ten atoms, have been observed in the gas phase. However, experimentally there are only a few stable small dianions,[6] consisting of less than ten atoms, including C_n^{2-} $(n=7-9)$,[20] $S_2O_6^{2-}$,[21] and most recently found, four penta-atomic dianions, PtX_4^{2-} and PdX_4^{2-} (X=C1 and Br).[19] Extensive theoretical work has been carried out on small gaseous multiply-charged anions such as alkali-halides (MX_3^{2-}),[22] mixed beryllium carbon dianions BeC_4^{2-} and BeC_6^{2-},[23] $Mg_2X_4^{2-}$,[24] and small carbon cluster dianions.[25–27]

On the other hand, it has been shown recently that superintense radiation fields of sufficiently high frequency can have large effects on the structure, stability, and ionization of atoms.[28–33] One of the most intriguing results of Gavrila and his co-workers is the possibility to have multiply charged negative ions of hydrogen by superintense laser fields.[34] This kind of stabilization phenomena has not been observed so far by any experiment, due to the need for superintense radiation fields. There are, however, experiments demonstrating light-induced stabilization against photoionization when the atom is initially prepared in a Rydberg state.[35]

A classical interpretation for the stabilization which enables an atom to bind many additional electrons has been given by Vorobeichik *et al.*[36] They showed that for sufficiently large value of $\alpha_0=E_0/\omega^2$, where E_0 and ω are the amplitude and frequency of the laser field, the frequency associated with the motion of the particle in the time-averaged potential V_0, is much smaller than the laser frequency and, therefore, the mean field approach is applicable.

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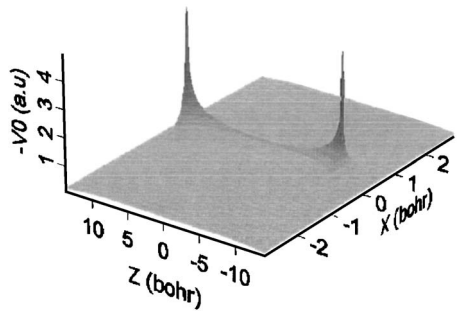

FIG. 1. The dressed Coulomb potential, $-V_0(r,\alpha_0)$, for the He at $\alpha_0=11$.

Moiseyev and Cederbaum have shown that the stabilization effect takes place at increasing field strengths when first, the photoionization rate decreases and second, electron correlation and hence autoionization is suppressed.[38] For one-electron atoms/ions, Pont *et al.*[37] have shown that by increasing α_0, the electronic eigenfunctions of the "dressed" potential of an atom in high intense laser field and the corresponding charge densities are split into two lobes located around the end points of the nuclear charge, which is smeared along a line. This phenomenon has been termed a dichotomy of the atom. Within the framework of the dipole approximation, the two charges are equal to half the atomic nuclear charge and are separated by a distance $R=\sqrt{2}\alpha_0$. Transferring this approximation to the helium atom in strong laser fields, it is described as a "hydrogen molecule" where the distance between the two "hydrogen atoms" is controlled by the field intensity. It is known in quantum chemistry that the electronic correlation is reduced in the course of the breaking of a chemical bond. Namely, atoms in high intense linearly polarized laser fields behave like homonuclear diatomic molecules where the bond length can be controlled by the laser field intensity. For sufficiently high laser intensity, "dissociation" takes place due to the suppression of the electronic correlation and an atom with atomic number Z behaves in a high intensity laser field as two separate virtual atoms each one of them associated with an effective atomic number $Z/2$. For example, the helium atom in a sufficiently strong linear laser field behaves like two virtual noninteracting hydrogens and therefore can bind one or even two more electrons since H^- has a ground bound state. This idea stands behind our present work. Here we carry out *ab initio* calculations for many electron atoms where the full electronic correlation is taken into consideration. The interaction with the laser field is taken into consideration by including the exact expression of the dressed potential in our numerical calculations.

A monochromatic field of electric field vector has the following form: $\mathbf{E}(t)=E_0(\mathbf{e_1}\cos\omega t+\mathbf{e}_2\tan\delta\sin\omega t)$ with $\mathbf{e}_j$ $(j=1,2)$ unit vectors orthogonal to each other and to the propagation direction, $\delta=0$ corresponds to linear polarization, and $\delta=\pm\pi/4$ to circular polarization. The high-frequency Floquet theory proceeds from the space translated version of the time-dependent Schrodinger equation which for N-electron atoms reads[28]

$$\sum_{i=1}^{N}\left[\frac{1}{2}\mathbf{P}_i^2-\frac{Z}{|\mathbf{r}_i+\alpha(t)|}+\sum_{j=1}^{i-1}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right]\Psi=i\frac{\partial\Psi}{\partial t}, \tag{1}$$

where $\alpha(t)=(\alpha_0/E_0)\mathbf{E}(t)$ with $\alpha_0/E_0=1/(m_e\omega^2)$. This equation refers to a coordinate frame translated by $\alpha(t)$ with respect to the laboratory frame. By using the Floquet ansatz one seeks to determine solutions to the following structure equation[28]

$$\sum_{i=1}^{N}\left[\frac{1}{2}\mathbf{P}_i^2+V_0(\mathbf{r}_i,\alpha_0)+\sum_{j=1}^{i-1}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right]\Phi=\epsilon(\alpha_0)\Phi. \tag{2}$$

Here V_0, the "dressed" Coulomb potential, is the time average of $-Z/|\mathbf{r}+\alpha(t)|$,

$$V_0(\mathbf{r},\alpha_0)=-\frac{Z}{2\pi}\int_0^{2\pi}\frac{d\xi}{|\mathbf{r}+\alpha(\xi/\omega)|}. \tag{3}$$

For linear polarization, the "dressed" potential V_0 is equivalent to that of a linear charge with a relative larger charge density near the two end points and a smaller one

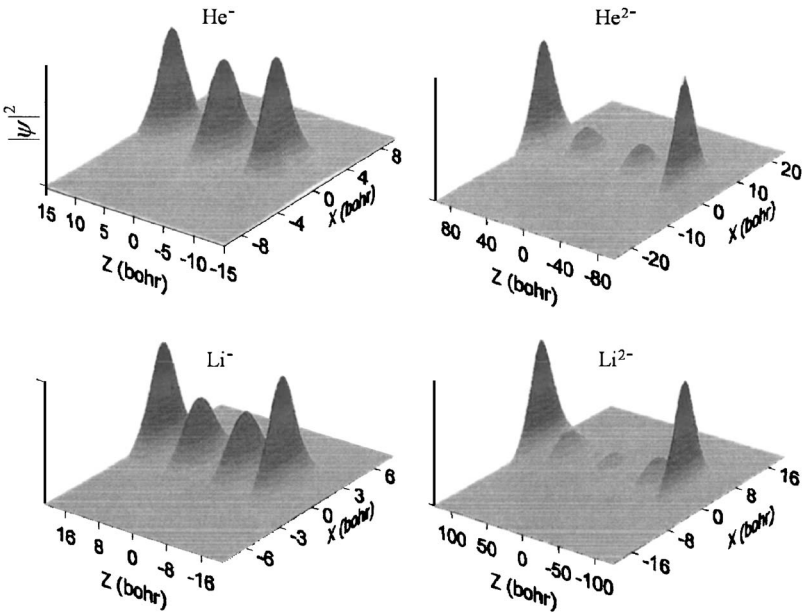

FIG. 2. Electronic charge distribution for He^-, He^{2-}, Li^-, and Li^{2-} in linearly polarized (along the z axis) laser fields at their $\alpha_0^{\text{critical}}=11,82,16$, and 105 a.u., respectively. Note that there is no overlap of the orbitals.

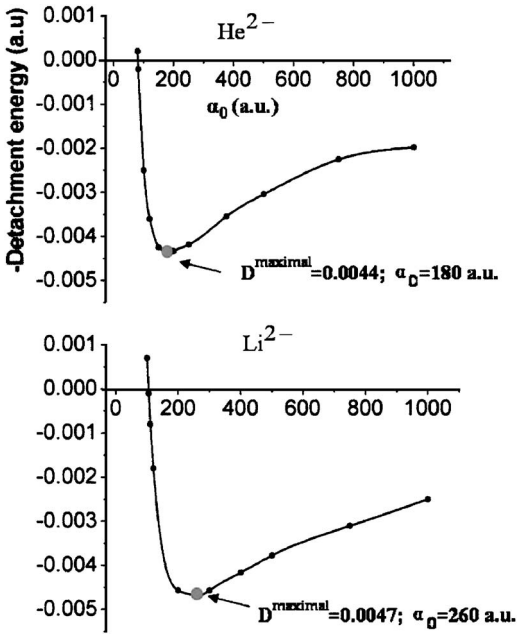

FIG. 3. Negative of the detachment energy (in a.u.) of the ground state of He^{2-} and Li^{2-} in a linearly polarized high-frequency laser field as a function of $\alpha_0=E_0/\omega^2$, where E_0 and ω are the amplitude and frequency of the laser field. The maximum values of $\alpha_0^{\text{maximum}}$ are given along with the detachment energies.

near the center. The length of the linear charge is $2\alpha_0$. In a two-center coordinate system, V_0 has the following form:

$$V_0(\alpha_0,r)=-\frac{2Z}{\pi}(r_A\cdot r_B)^{-1/2}K\left[\left(\frac{1-\hat{r}_A\cdot\hat{r}_B}{2}\right)^{1/2}\right], \tag{4}$$

where A and B are the two foci of the system (two end points of the linear charge). Z is the nuclear charge and K is elliptical integral of the first kind. In Fig. 1 we show the potential $V_0(\alpha_0,r)$ along the polarization field direction for He at fixed value of $\alpha_0=11$ a.u. This functional form is typical for all systems used in this report.

Since it is a two-center system, the standard basis sets of elliptical functions are used here and have the following form:

$$\Phi(\xi,\eta,\phi)_{p,q,m}=(\xi-1)^p\eta^q[(1-\eta^2)(\xi^2-1)]^{m/2}e^{-\gamma\xi}e^{im\phi}, \tag{5}$$

where p, q, and m are non-negative integers, and γ is a variational parameter which will be used to optimize the numerical results, and ξ, η, and ϕ are prolate spheroidal coordinates with $\xi=(r_A+r_B)/2\alpha_0$ and $\eta=(r_A-r_B)/2\alpha_0$.

Now we can proceed by using the self-consistent field method to obtain the ground state energy and wave function of a given atom with a nuclear charge Z in a laser field. Then we find the critical value of α_0 for binding N-electrons to such a given atom. As long as $\epsilon^{(N)}(\alpha_0)>\epsilon^{(N-1)}(\alpha_0)$, one of the electrons on the N-electron ion autodetaches and therefore the atomic multiply charged negative ions are unstable. In order to determine the stability of an atomic multiply charged negative ion, we define $\alpha_0^{\text{critical}}$ for which the detachment energy $D^{(N)}(\alpha_0^{\text{critical}})=0$. The detachment energy is the energy required to detach one of the N electrons from an ion at a particular value of α_0, $D^{(N)}(\alpha_0)=\epsilon^{(N-1)}(\alpha_0)-\epsilon^{(N)}(\alpha_0)$. Therefore we can find the critical value of α_0 for which $D^{(N)}(\alpha_0^{\text{critical}})=0$. For values of α_0 larger than the $\alpha_0^{\text{critical}}$, none of the N electrons will autodetach, and the N-electron atomic multiply-charged negative ion supports a bound state.

We evaluated all the matrix elements by numerical methods. By self-consistent field methods we finally obtain the ground state energies and wave functions of He^-, He^{2-}, Li^-, and Li^{2-} which are shown in Fig. 2. Note that Li^- does exist in a field-free space; it was included only for comparison. We start the self-consistent field calculation by fixing all electrons with the same distance along the linear charge and it takes only a few iterations to reach equilibrium. We used a basis set of 81 basis functions which is accurate enough to describe the ground state wave function of these systems. It turns out that there is no overlap between the orbitals of different electrons as seen in Fig. 2, so the spin exchange term is not considered here. Finally we obtained the critical laser parameters to make He^-, He^{2-}, Li^-, and Li^{2-} bound. They are 11, 82, 16, and 105 a.u., respectively. That means He^-, He^{2-}, Li^-, and Li^{2-} will be in bound states when the α_0 of the laser field is larger than their critical parameters. When α_0 of the laser field is large enough, these systems can bind even more electrons.

The detachment energy as a function of α_0 for He^{2-} and Li^{2-} is shown in Fig. 3. It is interesting to see the resemblance of the detachment energy curves to the potential energy curves for their equivalent diatomic molecules. $\alpha_0^{\text{maximum}}$ is the α_0 with maximal detachment energy. The values are listed in Table I, which are 26, 180, 42, and 250 a.u. and the detachment energies at these points are 1.2, 0.12, 1.2, and 0.13 eV for He^-, He^{2-}, Li^-, and Li^{2-}, respectively. The fields and frequencies needed for binding extra electrons are within experimental reach. For example, when ultra-high-power KrF laser (5 eV photons) are used, the peak intensity in the experiments should be $I\approx 10^{16}W/\text{cm}^2$ (see Table I). The high

TABLE I. Critical parameters for stability of He^-, He^{2-}, Li^-, and Li^{2-} in superintense laser fields. The intensity is determined by the following equation: $I(W/\text{cm}^2)=|E_0(\text{a.u.})|^2\times 3.509\times 10^{16}$, where $E_0=\omega^2\alpha_0$, we choose $\omega=5$ eV, see the text for more details.

	$\alpha_0^{\text{critical}}$(a.u.)	$I^{\text{critical}}(W/\text{cm}^2)$	$\alpha_0^{\text{maximum}}$(a.u.)	$I^{\text{maximum}}(W/\text{cm}^2)$	Detachment energy (eV)
He^-	11	4.8×10^{15}	26	2.7×10^{16}	1.2
He^{2-}	82	2.7×10^{17}	180	1.3×10^{18}	0.12
Li^-	16	1.0×10^{16}	42	7.1×10^{16}	1.2
Li^{2-}	105	4.4×10^{17}	260	2.7×10^{18}	0.13

frequency field approximation holds when the field oscillates much faster than the electrons, $\omega_e/\omega_L \ll 1$. On the basis of semiclassical arguments we estimate the electron motion frequency by calculating the electronic excitation of the atom in the presence of the field, $\omega_e=(E_1-E_0)/\hbar$. The excitation energy for He^- is 1.3 eV and for Li^-, 2.04 eV which is smaller than the laser frequency 5 eV. For He^{--} and Li^{--} the ω_e/ω_L is much smaller than the He^- and Li^-. Therefore, our results clearly show that we are indeed in the high frequency regime and the electronic oscillations in the presence of the strong laser field are much smaller than the laser frequency. At such high frequency the time-averaged "dressed" potential, V_0, is the dominant term and therefore this approach is applicable. When free electron lasers are used the frequency gets much larger values and the superintense laser fields should be applied.

In summary, we predicted new stable multiply-charged negative atomic ions in linearly polarized superintense laser fields. This method of stabilization is general, within experimental reach and can be used to predict stability of larger multiply-charged negative atomic ions.

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