

## Quantum States of Magnetically Induced Anions

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(Received 11 May 2005; published 8 September 2005)

In a magnetic field, an atom (or molecule) can attach an extra electron to form an unconventional anionic state which has no counterparts in field-free space. Assuming the atom to be infinitely heavy, these magnetically induced anionic states are known to constitute an infinite manifold of bound states. In reality, the species can move and its motion across the magnetic field couples to the motion of the attached electron. We treat this coupling, for the first time, quantum mechanically, and show that it makes the number of bound anionic states finite. Explicit numerical quantum results are presented and discussed.

DOI: 10.1103/PhysRevLett.95.113002

PACS numbers: 31.10.+z, 31.15.Ar, 32.10.Hq

For many decades, negative ions have remained in the focus of intense research, both theoretical and experimental (see, e.g., [1–4], and references therein). This continuous interest is due to the relevant role negative ions play in a variety of physical and chemical processes, e.g., in stellar and terrestrial atmospheres, in interstellar clouds, and in plasmas [5,6]. The formation and binding mechanisms of negative ions are of a delicate nature. Most neutral atomic and small molecular species lead to anions with a single or at most a few bound states. A typical example is the atomic hydrogen anion which possesses a single valence-bound state [7,8]. In some cases even no anionic counterparts exist [3].

Negative ions in external fields are of particular interest. Calculations show that when being exposed to a magnetic field, the hydrogen anion also exhibits an excited valence-bound state (see, e.g., [9] and references therein). Even more intriguing is the mathematical prediction [10] that *any* atomic anion possesses *infinitely many* bound states in a magnetic field of *arbitrary* strength. This prediction has stimulated investigations [11–14] of anions formed *exclusively* due to the presence of a magnetic field which we refer to as *magnetically induced anions*. In deriving the mathematical prediction, it was assumed that the nuclei are infinitely heavy [10]. Since in reality the center of mass does not decouple from the internal motion in a magnetic field [15,16], two major issues remain puzzling: (i) is the number of the anionic bound states indeed infinite and (ii) what are the actual binding energies of these states. The first question has been answered before using arguments of classical dynamics [12]. In this work we confirm this answer and provide quantum results for the binding energies of some experimentally relevant magnetically induced anions.

Let us first describe the binding properties of anions in magnetic fields assuming that the nuclei are infinitely heavy, i.e., fixed in space. In the underlying physical picture [4,11] an excess electron is nonvalence bound occupying an extended orbital which is confined by the magnetic field. The electron can only escape in the direc-

tion along the field, which makes the problem of its binding by the *static* neutral species essentially *one dimensional*. The longitudinal angular momentum of the attaching electron represents an *integral of motion*,  $l_z = -s$ ,  $s = 0, 1, 2, \dots$ . For each  $s$  a specific one-dimensional potential  $V_s(z)$  supports a bound longitudinal motion in a specific quantum state. Consequently, an infinite manifold of bound states appears. For those neutral species which do not possess a permanent dipole moment the nature of the potentials  $V_s(z)$  is a polarization attraction of the excess electron. The corresponding binding energies were explicitly evaluated in [11]:

$$\begin{aligned} \varepsilon_0 &= 0.31\kappa^2 B^2, & s &= 0, \\ \varepsilon_s &= 0.12\kappa^2 B^3 \delta_s^2, & s &= 1, 2, \dots, \\ \delta_1 &= 1, & \delta_s &= [1 - (1.5/s)]\delta_{s-1}, \end{aligned} \quad (1)$$

where  $\kappa$  is the polarizability of the species and  $B$  is the magnetic field strength, both in atomic units.

Let us note that the above physical picture should be applied with care to the magnetically induced state with  $s = 0$ . This state typically possesses the same symmetry as the conventional anionic state in case the latter exists. Therefore, the  $s = 0$  state can only manifest itself for species which do not form stable anions without the magnetic field [4]. This is in agreement with the variational calculations of the magnetically induced states formed by the attachment of an electron or positron to a neutral hydrogen atom [14].

The assumption that the anion is infinitely heavy turns out, however, to be too crude when treating magnetically induced anions. It neglects an important detachment channel—the possibility for the neutral species to move away transverse to the field from the excess electron. Considerations in the framework of classical dynamics have shown that the motion of the neutral species possesses a severe impact on the spectral and dynamical properties and on the mere existence of the magnetically induced

anions [12]. In the following we provide results of the quantum treatment of the problem.

The excess electron in a magnetically induced anion is loosely bound and occupies an extended orbital [4]. At laboratory field strengths this orbital exceeds by orders of magnitude the typical size of an atom or molecule. This allows one to safely neglect pure correlations and spin-orbit coupling of the extra electron with the electrons of the underlying neutral system. The extra electron interacts with a neutral species (e.g., an atom) of mass  $m_{\text{at}}$  via a polarizationlike attraction. For such an effective two-body problem in a magnetic field, the collective motion along the field as well as the motion of the guiding center of the system in a transverse direction can be decoupled from the other motions. In addition, the fast Larmor rotation of the extra electron can be averaged out [12]. The remaining *three* degrees of freedom relate to a one-dimensional motion of the atom relative to the decoupled guiding center and to a two-dimensional motion of the excess electron relative to the atom. The corresponding canonical pairs of coordinates and momenta are  $\{Q, P\}$ ,  $\{q, p\}$ , and  $\{z, p_z\}$ , respectively. The final Hamiltonian reads [12]

$$\begin{aligned} H(Q, P; q, p; z, p_z) &= H_1(Q, P; q, p) + H_2(Q, P; z, p_z), \\ H_1(Q, P; q, p) &= \frac{\Omega}{2}[(P + q)^2 + (Q + p)^2], \\ H_2(q, p; z, p_z) &= \frac{p_z^2}{2\mu} + V_{\text{eff}}(z^2, r_c^2), \end{aligned} \quad (2)$$

where  $\Omega = B/m_{\text{at}}$  and  $\mu = m_{\text{at}}m_e/(m_{\text{at}} + m_e)$  is the reduced mass of the extra electron. The effective potential  $V_{\text{eff}}$  links the excess electron to the atom and is given in closed form in [12]. It depends on the longitudinal,  $z$ , and transverse,  $r_c$ , displacements of the electronic guiding center from the atom. The latter quantity is represented by the operator  $r_c^2 = (q^2 + p^2)/B$ . The zero energy shell,  $H = 0$ , corresponds to the detachment threshold for the magnetically induced states. It separates the bound states with negative eigenvalues of the Hamiltonian (2) from the detaching (continuum) states with positive energies.

For a moving anion, the longitudinal angular momentum of the excess electron is no longer an integral of motion. Instead, the total angular momentum along the field is conserved. The corresponding operator

$$\mathcal{L} = \frac{1}{2}(Q^2 + P^2 - q^2 - p^2) \quad (3)$$

has integer eigenvalues  $J$  which conveniently label the magnetically induced states.

In the Hamiltonian (2), the degrees of freedom of the atom and the excess electron are coupled to each other. This results from the coupling of the internal degrees of freedom to the collective motion of a quantum system in a magnetic field. Although the Hamiltonian (2) with its 3 degrees of freedom has a reasonably low dimension, its quantum treatment is nontrivial because of the dependence

of the effective potential on the momentum  $p$  which renders the potential nonlocal. For the *ab initio* description of the discrete eigenstates of the Hamiltonian (2) we apply basis functions which comprise two sets of functions:

$$\Phi_n^{(J)}(Q, q) = i^{-n} \mathcal{H}_{J+n}(Q) \mathcal{H}_n(q) \quad (4)$$

with  $n = 0, 1, 2, \dots, J = -n, -n + 1, -n + 2, \dots$  and

$$\varphi_\nu^{(\alpha)}(z) = \sqrt{\alpha} \exp(-\alpha|z|) L_\nu(2\alpha|z|) \quad (5)$$

with  $\nu = 0, 1, 2, \dots$ . The functions (4) are constructed from the eigenfunctions of a one-dimensional harmonic oscillator,

$$\mathcal{H}_n(q) = \frac{\exp(-q^2/2)}{\sqrt{2^n n! \sqrt{\pi}}} H_n(q), \quad (6)$$

where  $H_n$  are the Hermite polynomials. In Eq. (5),  $L_\nu$  are the Laguerre polynomials and  $\alpha$  is a parameter which allows one to adjust the basis functions to the longitudinal spatial extension of a state of interest (see below).

Let us notice a few properties which make the basis functions introduced above convenient for calculating the quantum states of the Hamiltonian (2). The action of the nonlocal potential on the functions (4) can be evaluated analytically [13] providing a diagonal matrix

$$\langle \Phi_n^{(J)} | V_{\text{eff}}(z^2, r_c^2) | \Phi_s^{(J)} \rangle = V_s(z) \delta_{n,s}, \quad (7)$$

where  $V_s(z)$  are the potentials mentioned above Eq. (1). They guide the motion of the excess electron in the states of the static, i.e., infinitely heavy, magnetically induced anion. The functions (4) are the eigenfunctions of the total longitudinal angular momentum,  $\mathcal{L}\Phi_n^{(J)} = J\Phi_n^{(J)}$ , which attributes the *ab initio* states to the quantized values of the integral of motion (3). The functions (5) are well suited for describing the motion of a loosely bound electron along the magnetic field. In particular, the functions with  $\nu = 0$  and with the values  $\alpha_s = \sqrt{2\varepsilon_s}$  for the parameter  $\alpha$  mimic the wave functions of the magnetically induced states of the infinitely heavy anion.

The sets of basis functions (4) and (5) are orthonormal and complete. Applying them reduces the search of the discrete eigenstates of the Hamiltonian (2) to a standard eigenvalue problem for the real symmetric matrix composed of the elements  $\langle n' \nu' | H | n \nu \rangle$ . In our calculations, we have extended the number of basis states until convergence of an eigenenergy of interest is achieved. As the basis functions are  $L^2$  functions, we can only study the bound states of the Hamiltonian (2).

As a first application of our approach, we have studied the magnetically induced anionic states of noble gas atoms and of other related atoms. Because of their electronic structure, these atoms are known to be unable to form stable anions in field-free space and are good candidates to provide  $s = 0$  magnetically induced states.

Diagonalizing the matrix form of the Hamiltonian (2), we have numerically obtained the negative eigenenergies for different values of  $J$  which enumerate the *motional ground and excited states* of the anion. We have found the excitations to form a few branches. Their number depends on the magnetic field strength. In some situations only a single branch of bound states exists or even none. In order to connect the results to the case of the infinitely heavy anions, we enumerate these branches by  $s = 0, 1, 2, \dots$ . The numbers  $s$  and  $J$  label the quantum energies,  $E_{sJ}$ , of the moving magnetically induced anions. For the infinitely heavy anions, these energies become independent on  $J$  and correspond to the binding energies (1),  $E_{sJ} \rightarrow -\varepsilon_s$ . This can be readily revealed from the limit  $m_{\text{at}} \rightarrow \infty$  equivalently  $\Omega \rightarrow 0$  for the Hamiltonian (2). When calculating the states associated with an  $s$  branch, we were adjusting the spatial extensions of the functions (5) by selecting  $\alpha = \alpha_s$ . Although these functions form a complete set for any value of  $\alpha$ , such “optimal” values were found to provide the desired numerical accuracy of the energies  $E_{sJ}$  at the minimum number of basis functions used.

In Fig. 1 we present the branches of the motional magnetically induced states of atomic anions which do not exist in field-free space. Two values of the magnetic field strength,  $B = 10$  T and  $B = 100$  T, are selected. For a branch  $s$ , the quantum number  $J$  can vary as  $J = -s, -s + 1, -s + 2, \dots$ . Because of the significant differences of the binding energies of the anions, it is convenient to plot the ratios  $E_{sJ}/\varepsilon_s$  against the values  $(\Omega/\varepsilon_s)(J + s)$ . The energies of the bound states grow with  $J$  which reflects the increasing energies of Larmor-like rotations of the anions bound in the magnetic field. As a result, increasing  $J$  finally turns the bound states into *autodetaching states* with positive energies.

For the branches shown in Fig. 1, the dependencies of the anionic energies on  $J$  are almost linear and fairly well approximated by a simple formula

$$E_{sJ} = (m_{\text{at}}/M_{\text{eff}})[- \varepsilon_s + \Omega(J + s)] \quad (8)$$

with a single fit parameter  $M_{\text{eff}}$ . This parameter has a meaning of an effective mass of the bound anion and was found to be different for different  $s$  branches of the motional states. It depends on the properties of the neutral species (mass and polarizability) as well as on the magnetic field strength.

At a typical strong laboratory magnetic field strength of 10 T, all studied atoms but one exhibit a single branch ( $s = 0$ ) of magnetically induced anionic states. The exception is the lightest He atom which is found not to possess a bound state. This atom has also the smallest polarizability which turns out to be insufficient to support a bound anionic state at this magnetic field strength. This example clearly demonstrates the effects of finite atomic mass. For all the other atoms studied in Fig. 1 there exist bound states with energies  $E_{0J} \approx -\varepsilon_0 + \Omega J < 0$ . These represent the mo-

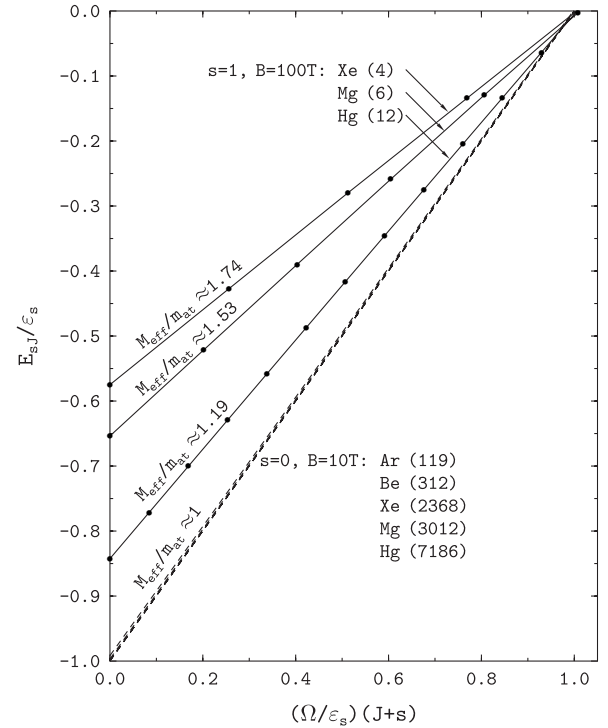


FIG. 1. Energies of the motional magnetically induced anions formed by atoms which do not form anions in field-free space. Dashed lines show the  $s = 0$  branches of excitations for  $B = 10$  T. Dots show the quantum levels with  $s = 1$  and different values of  $J$  for  $B = 100$  T, and are connected by solid lines for visualization of the analytical approximation (8). Also indicated in the figure are the numbers of the bound motional states along the branches (in parentheses) and the effective anionic masses (near the solid and dashed lines).

tional excitations of the  $s = 0$  state of the infinitely heavy anions. The higher  $s$  states are completely destroyed by the motional effects. It is worthy to notice the quite significant (although finite) number of motional excitations in the  $s = 0$  branch and that this number strongly depends on the atom and on the field strength. Also note that the effective masses of the anions practically coincide (for  $s = 0$ ) with the masses of the corresponding neutral atoms.

At a significantly higher field strength of 100 T, we encounter for the three atoms, Xe, Mg, and Hg, in addition to the  $s = 0$  branch the appearance of the  $s = 1$  branch of magnetically induced states. The number of bound motional states in this branch is rather small: 4, 6, and 12, for Xe, Mg, and Hg, respectively. Here, the bound  $\text{Xe}^-$  anion displays the biggest ratio,  $\approx 1.74$ , of the effective mass  $M_{\text{eff}}$  to the mass of the neutral atom. This anion also shows the largest relative deviation of the binding energy of the  $s = 1, J = -1$  state from the corresponding binding energy  $\varepsilon_1$  of the infinitely heavy anion.

For infinite nuclear mass an infinite manifold of bound states was predicted in [10] to exist for arbitrarily small magnetic field strength. In reality, states can only be bound

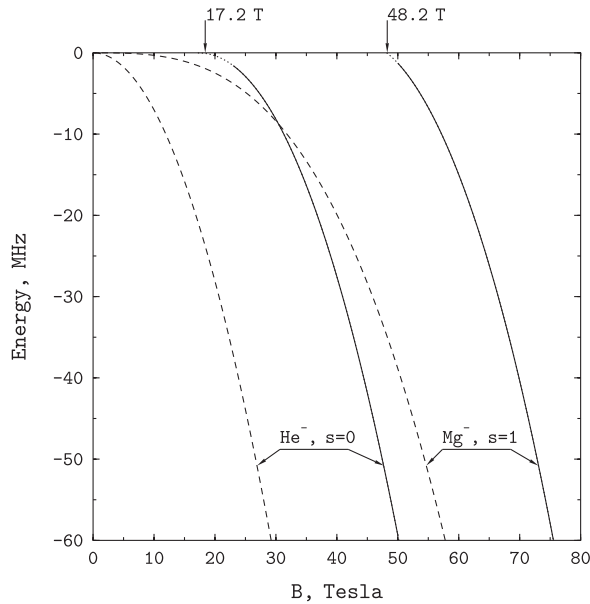


FIG. 2. The energy of the lowest bound state of the anion  $\text{He}^-$ , i.e.,  $s = 0$ ,  $J = 0$ , and of the state  $s = 1$ ,  $J = -1$  of  $\text{Mg}^-$ , as a function of the magnetic field strength (solid lines). Dashed lines show the corresponding energies of the infinitely heavy anions. Dots correspond to polynomial extrapolations of the solid lines towards the detachment threshold (zero energy). Arrows point to the minimum values of the field strength (indicated near the arrows) required to support a bound state.

for field strengths exceeding some critical values that depend on the species considered. This is demonstrated in Fig. 2 in terms of the energies of states with  $s = 0$  for the anion  $\text{He}^-$  and with  $s = 1$  for the anion  $\text{Mg}^-$ . The energies are shown as functions of the field strength and compared with the corresponding energies of the infinitely heavy anions. Due to the effects of finite atomic masses, the lowest bound state of  $\text{He}^-$  appears at  $B > 17.2$  T, and the lowest bound  $s = 1$  state of  $\text{Mg}^-$  is supported at  $B > 48.2$  T. Interestingly, these critical fields are close to the values previously indicated in [12] on the grounds of simple energetic arguments. At all field strengths higher than these critical values, the binding energies of the motional states are substantially smaller than those of the infinitely heavy anions.

To conclude, we have demonstrated that accounting for the quantum effects of the finite anionic mass has a dramatic impact on the manifold of the magnetically induced bound states: the majority of the infinite sequence of the states (1) become unbound, while each of the remaining bound states splits into a finite series of quantum motional excitations. For the anions of the noble gas atoms at laboratory field strengths, basically only the lowest  $s = 0$  magnetically induced state survives and is transformed into

a sequence of motionally excited states. Further studies which we expect to bring new fundamental knowledge on properties of quantum states of magnetically induced anions should concern autodetaching states. The  $J$  series shown in Fig. 1 terminate at  $E_{sJ} = 0$ , but can be thought of to continue into the range of positive energies where instead of bound states one may find metastable states. It is also very challenging to investigate anions formed by different interaction mechanisms with an excess electron. Relevant examples are small clusters or dipolar molecules where one could discover magnetically induced anionic states of species which do not form stable anions without the magnetic field.

Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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