Negative ions of inert gases

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Numerical calculations have been carried out on the basis of a model potential and relativistic perturbation theory with a model zeroth approximation. The results predict the existence of stable negative ions of inert gas atoms: Kr^{*-} and Xe^{*-}.

It has been the belief that inert gas atoms do not form stable negative ions.[1] The only exceptional case is the He atom, which has the negative ion $He^- 1s2s2p^4P$ (Refs. 2–4). This long-lived state ($\gtrsim 10^{-5}$ s) forms when an electron attaches to an $He1s2s^3S$ atom in a metastable state. The measured electron affinity of He^3S is 77.5 ± 1. A calculation carried out in Ref. 3 yielded a result in excellent agreement with this value.

In this letter we present a calculation which shows that not only the He^3S but also some heavier inert gas atoms, $Kr^*4p_3^5s^3P$ and $Xe^*5p^56s^3P$ in a low-lying excited state, form stable negative ions with the configuration $np^5(n+1)s(n+1)p$. We must assume that the stable negative ions with the configuration $np^5(n+1)s(n+1)p$ form by virtue of a strong polarization potential acting between the electron and the atom. The potential is in turn due to the large dipole polarizability of the atoms:[1] $\alpha(Kr^{*3}P) = 341$ a.u. and $\alpha(Xe^{*3}P) = 426$ a.u. The following values are found for the binding energies of an electron in the Kr^{*-} and Xe^{*-} ions: $EA(Kr^*) = 0.12$ eV and $EA(Xe^*) = 0.16$ eV. These calculations use a method involving a polarization potential and a relativistic perturbation theory with a model zeroth approximation. This approach has been taken successfully in previous precise calculations for various

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atoms, multiply charged ions, and negative ions.[6–13] A test of this method through a calculation of the binding energy of an electron in the negative ion Na^- confirmed that this method has a completely acceptable accuracy.[14]

In order to determine the stability of the negative ions of interest and to find the electron affinities of the atoms, we need to calculate the ground-state energies of the Kr^{*-} and Xe^{*-} ions. We also need the energies of the neutral atoms in their first excited state. A correct calculation for Kr^{*-} and Xe^{*-} requires an accurate account of electron-electron correlations. We deal with these correlations by a relativistic perturbation theory with a model zeroth approximation, as effects of higher-order perturbation theories (starting with the second order). As usual, the energy matrix is calculated in the scheme of j–j coupling of the angular momenta. We go over to the intermediate coupling scheme through a diagonalization of a secular matrix. The states of interest of the negative ions and the states of the corresponding neutral excited atoms can be treated as three-particle and two-particle states [states with two electrons and one vacancy and with one electron and one vacancy outside the core (and inside the core) of filled electron shells with the following ground-state configuration of the inert gas atoms: $Kr4p^6\ ^1S$, and $Xe5p^6\ ^1S$]. The energies of these states are written as perturbation-theory series:[6,10,13,15]

$$E(n_1l_1j_1, n_2l_2j_2, n_3l_3j_3) = \sum_{i=1}^{3} \epsilon^{(0)}(n_il_ij_i) + \Delta E^{(1)} + \Delta E^{(2)} + \dots ,$$

$$E(n_1l_1j_1, n_2l_2j_2) = \sum_{i=1}^{2} \epsilon^{(0)}(n_il_ij_i) + \Delta E^{(1)} + \Delta E^{(2)} + \dots .$$

Here $\epsilon^{(0)}$ are the one-particle energies of an electron outside a core (of a vacancy inside a core), which are determined by the first ionization potentials of the Rb and Cs atoms, respectively, and by the transition energies of an electron outside the Rb and Cs cores [by the first ionization potentials of the inert gas atoms $Kr(^1S)$ and $Xe(^1S)$; Refs. 1 and 16]. Here also, $\Delta E^{(i)}$ is the ith-order perturbation-theory correction. The one-particle energies $\Sigma_i \epsilon^{(0)}(n_il_ij_i)$ contribute to only the diagonal elements. The empirical information embodied in the zeroth approximation (more on this below) contains a large fraction of the correlation and relativistic effects. The zeroth-approximation one-particle wave functions are found through a solution of the Dirac equation. This equation has the experimental energy of the electron, $\epsilon_{el}^{(0)}$ (or the vacancy, $\epsilon_{vac}^{(0)}$) as an eigenvalue. The model potential describing the interaction of the outer electron (or vacancy) with the core was taken to be[17]

$$V_M(r) = -\frac{1}{r} + \frac{A}{r}e^{-2kr},$$

where A and k are adjustable parameters of the potential (for the Rb atom, $A + 1.640$ and $k = 0.358$; for the Cs atoms, $A = 1.672$ and $k = 0.333$). The perturbation operator is

$$H_p = \sum_{i>j} r_{ij}^{-1} - \sum V_M(r_i).$$

The first order of the perturbation theory (the correction $\Delta E^{(1)}$) is determined by the matrix element of the operator r_{ij}^{-1} between the wave functions of the outer particles alone. Two-particle relativistic interactions of the outer particles are ignored, since they contribute only a small correction. In first-order perturbation theory there is no matrix element from the compensating part of the potential, V_M, in H_p. Matrix elements of V_M do appear in second-order perturbation theory, but their contribution is canceled to a large extent by a contribution from diagrams with so-called Hartree–Fock inserts, as was shown by Tolmachev[8] (see also Refs. 6 and 7). The most important contribution from the core polarization and the mutual screening (or antiscreening) of the outer particles comes from the two-particle second-order diagrams

$(P_1 =$  ,

which is the direct polarization diagram;

$P_2 =$  ,

which is the inverse polarization diagram; and

$S_1 =$  ,

which is the direct ladder diagram). These diagrams are usually dealt with by expanding to the secular matrix, i.e., by finding additional states of two types: (a) states with an excitation of particles from the core (diagrams P_1 and P_2) and (b) states corresponding to the excitation of one of the outer particles (with a "frozen" core; diagrams of the type S_1). Some effective methods for dealing with states of both types, without an increase in the dimensions of the secular nature, were proposed and described in detail in Refs. 13 and 15. They involve adding an additional polarization potential to the operator representing the electron-electron Coulomb interaction, $e^{i\omega r_{12}}/r_{12}$ ($e^{i\omega r_{12}}$ is a factor incorporating retardation). This additional potential describes the interaction of the outer particles through the polarized core [states of type (a)]. A correct polarization potential (a two-particle potential) was proposed in Ref. 15 (see also Refs. 14 and 18). A special screening potential, proposed in Ref. 15, was introduced in the zeroth approximation of the perturbation theory in order to deal with the screening of the outer particles by each other [states of type (b)]. This potential was then subtracted from the perturbation operator in a natural way. This method for dealing with polarization and screening effects leads to quite accurate results in the sense that it incorporates these effects comprehensively, as has been shown by numerous calculations. The most difficult point in the calculation of the energy matrix is calculating the angular parts of the matrix elements which arise during the integration over the angular variables and during the summation over the spin variables. We used the Fano method and the Berk algorithm here. We might add that in the case of three-particle states the matrix elements of the perturbation operator were constructed from the wave functions for these states and were expressed in terms of matrix elements calculated between two-particle states (they are described in detail in Ref. 13).

In the present calculations of the electron binding energies in negative ions of inert gas atoms we found the following results: $EA(\mathrm{Kr}^{*}\,{}^{3}P) = 0.12$ eV and $EA(\mathrm{Xe}^{*}\,{}^{3}P) = 0.16$ eV. Consequently, this calculation predicts the existence of stable negative ions of inert gases: Kr^{*-} and Xe^{*-}. This prediction is at odds with the current beliefs. Extensive experience in the use of the method of relativistic perturbation theory with a model zeroth approximation has shown that the error in the calculations of the energy spectra of atoms and multiply charged and negative ions seldom exceeds 1000–2000 cm^{-1} (there are some exceptional cases). In calculations on two- and three-particle systems, the value found for the binding energy is probably higher than the possible calculation error, by virtue of the cancellation of the error in the difference between the energies of these states.

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