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LETTER TO THE EDITOR

Yb^- $6p_{1/2}$—low-lying shape resonance rather than a bound state

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Abstract. Strong evidence against stability of the negative ion of ytterbium is presented, and the prediction is made that the lowest negative ion state Yb^- $4f^{14}6s^26p\ ^2P_{1/2}$ is a narrow shape resonance in the electron–atom continuum at 20 meV. These results are obtained from the many-body theory calculations with the electron–atom correlation potential appropriately scaled to reproduce the experimental data for the isoelectronic neutral Lu and Ba^-. They are in agreement with the recent thorough experimental investigation of Yb^- by the Aarhus group.

The aim of this letter is to show that contrary to earlier theoretical evidence, the ytterbium negative ion is most likely unstable, and the ns^2np negative ion configuration represents a $p_{1/2}$-wave shape resonance in the electron–atom continuum at about 20 meV. Our calculation confirms the recent experimental work by Andersen *et al* (1998) that has found no evidence for the existence of stable or long-lived metastable Yb^-.

Before 1987 the only negative ion known to be formed by a closed-shell atom was Pd^- $4d^{10}5s$ (Hotop and Lineberger 1985). Together with neutral Pd with its unique d^{10} ground-state configuration, this ion looked to be an exception to the rule. This rule had to change following the discovery of the stable Ca^- negative ion (Froese Fischer *et al* 1987, Pegg *et al* 1987) and a number of theoretical papers where heavier alkaline-earth atoms were predicted to be stable (Froese Fischer 1989, Gribakin *et al* 1989, Johnson *et al* 1989, Kim and Green 1989, Vosko *et al* 1989, Gribakin *et al* 1990).

A comparison of the second column ns^2 atoms shows (Gribakin *et al* 1990) that the binding of an extra electron into the open np subshell is ensured by the high atomic dipole polarizability α, which leads to a strong attractive polarization potential ($-\alpha e^2/2r^4$ at large distances) between the electron and the atom. The dipole polarizability of Ca is quite large, $\alpha(\mathrm{Ca}) = 170$ au, and those of Sr, Ba and Ra are even greater (Weast 1988). Accordingly, these atoms are capable of binding an extra electron into the ns^2np negative ion state. The polarizabilities of the other second column atoms (Be, Mg, Zn, Cd and Hg) do not exceed $\alpha(\mathrm{Mg}) = 72$ au, and they only have p-wave resonances at low energy (few tens of eV) in the electron–atom continuum.

A quick survey of the periodic table shows that there is just one more closed-shell atom, Yb $4f^{14}6s^2$, whose polarizability is close to that of Ca, $\alpha(\mathrm{Yb}) = 142$ au (Weast 1988). So, it came as no surprise that its negative ion was predicted to be stable in the two independent

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calculations by Vosko *et al* (1991) and Gribakina *et al* (1992). The former used a density functional theory approach and reported the electron affinity of 54 ± 27 meV. The latter applied the many-body theory Dyson equation method (nonrelativistic version) and obtained a value of 98.5 meV for the binding energy of the 6p electron in Yb^- $4f^{14}6s^26p$. A better relativistic Dyson equation calculation by Dzuba and Gribakin (1994) showed that only the lower $np_{1/2}$ fine-structure component was bound by 36 meV, whereas the unbound $p_{3/2}$ state manifested as a shape resonance in electron–atom scattering at 30 meV. The existence of stable Yb negative ions was supported by the accelerator mass spectroscopy observations by Litherland *et al* (1991) who estimated the Yb^- binding energy to be greater than 10 meV.

Most of the early calculations of the Ca^- binding energy produced values greater than the original experimental 43 ± 7 meV of Pegg *et al* (1987). When a new series of experimental studies (Walter and Peterson 1992, Haugen *et al* 1992, Nadeau *et al* 1992) indicated that the true value might be much lower, about 20 meV, it became clear that all predictions of the electron affinities of Sr and Ba probably overestimated the true values. A number of later calculations produced lower binding energies (e.g. van der Hart *et al* 1993, Sundholm and Olsen 1994, Sundholm 1995).

However, it would be fair to admit that none of the theoretical approaches could produce true *ab initio* binding energies with meV accuracy. There is a deep physical reason for this. The electron binding by a closed-shell atom is a 100% correlation effect. In the static approximation the atomic potential does not support the negative ion bound state, and there is only a p-wave shape resonance in the continuum. Electron correlations, which can be loosely thought of as polarization of the atom by the external electron, give rise to a strong attractive *correlation potential* between the electron and the atom. The Dyson equation method of many-body theory is an exact realization of this physical picture. It is easy to see within this method that for alkaline-earth negative ions most of the strength of the correlation potential (about 70–80%, Dzuba *et al* 1991) is 'wasted' on turning the p-wave resonance into a bound state at zero energy, and only the remaining 20–30% of it deepens the bound state to its actual position. This means that to be able to predict the binding energy with meV accuracy one would ideally need 0.1% accuracy in the calculation of the correlations. Besides that, relativistic effects are very important, since even a small fine-structure splitting of the np orbital looks significant compared to the small binding energy.

The situation with the alkaline-earth electron affinities remained uncertain until a series of precise measurements by the Aarhus group established their true values (Petrunin *et al* 1995, 1996, Andersen *et al* 1997). Moreover, for the first time both fine-structure components $J = \frac{1}{2}, \frac{3}{2}$ of the ns^2np negative ion states of Ca, Sr and Ba have been identified unambigously. Their binding energies indeed turned out to be much smaller than the early theoretical predictions.

The remaining two closed-shell ns^2 atoms where stable negative ions could be expected are Ra and Yb. If the accuracy of *ab initio* calculations of these ions is insufficient, then one might use the existing precise experimental data for Ca, Sr and Ba to tune the calculations and make more accurate predictions for Ra and Yb. This idea can be implemented in a consistent way within the relativistic many-body theory approach.

This approach is based on the quasiparticle Dyson equation, which describes the electron outside a closed-shell atomic core,

$$H_0\psi(\boldsymbol{r}) + \int \Sigma_E(\boldsymbol{r}, \boldsymbol{r}')\,\psi(\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}' = E\,\psi(\boldsymbol{r}). \tag{1}$$

Here E is the energy of the electron with respect to the core, $\psi(\boldsymbol{r})$ is the quasiparticle wavefunction of this electron, H_0 is the Dirac–Fock (DF) Hamiltonian of the core,

and $\Sigma_E(\boldsymbol{r}, \boldsymbol{r}')$ is the non-local energy-dependent *correlation potential*. It describes the interaction between the electron and the core beyond the static direct and exchange potentials included in H_0. The correlation potential can be presented as a perturbation-theory expansion in terms of the residual electron–electron interaction. The terms of the series are best described using diagrams. Equation (1) was first applied to negative ions in non-relativistic calculations by Chernysheva *et al* (1988) (He^- and Pd^-), and later used by Johnson *et al* (1989), Dzuba *et al* (1991), Dzuba and Gribakin (1994) and Salomonson *et al* (1996) (Pd^- and alkaline-earth negative ions). It was also successful in calculations of neutral atoms with one valence electron (see, e.g., Dzuba *et al* 1987, 1988, 1989).

The main contribution to $\Sigma_E(\boldsymbol{r}, \boldsymbol{r}')$ comes from the lowest- (second-) order diagrams. However, calculations of neutral atoms (see Dzuba *et al* 1988, 1989, Blundell *et al* 1990a, b for Cs and Tl, and Dzuba *et al* 1995 for Fr) and alkaline-earth negative ions (Dzuba and Gribakin 1997) show that the second-order approximation $\Sigma^{(2)}$ usually overestimates the true correlation potential by 10–20%.

There are some systematic ways of including dominant higher-order diagrams (Dzuba *et al* 1987, Blundell *et al* 1988, Salomonson *et al* 1996). They reduce the inaccuracy of the correlation potential to just a few per cent. However, the remaining error in the small binding energies of the alkaline-earth negative ions is still 10–20% (Salomonson *et al* 1996, Avgoustoglou and Beck 1997). In the case of Yb^- this inaccuracy is too large to make unambiguous conclusions about its stability. For example, it has been found in the all-order relativistic calculations of Avgoustoglou and Beck (1997) that the inclusion of higher-order corrections makes Yb^- unbound by 2 meV. Nevertheless, they conclude that 'the approximations ... made to make the treatment of the system [Yb^-] computationally manageable do not exclude the possibility of an electron affinity around 10 meV'.

There is an alternative to summing up higher-order terms in the correlation potential. Its magnitude can be gauged by introducing a scaling factor λ before the second-order correlation potential and comparing the results obtained with $\Sigma = \lambda\Sigma^{(2)}$ with some experimental data. The value of λ inferred from such a comparison can then be used to make predictions for analogous systems. We used this procedure recently and reproduced the experimental fine-structure intervals in Ca^-, Sr^- and Ba^- with 2.7, 0.02 and 0.5% accuracy, respectively (Dzuba and Gribakin 1997). We also made predictions that only the lowest $p_{1/2}$ fine-structure level of the Ra^- $7s^27p$ negative ion is bound at 100 meV, whereas the $p_{3/2}$ level is unbound by 16 meV and represents a resonance in the electron–atom continuum. A similar approach was used earlier by Dzuba *et al* (1983) to predict the ionization potential and lowest energy levels of Fr, and the accuracy of their numbers turned out to be an amazing 0.2%.

In this work we apply this procedure to prove that Yb^- is most certainly unbound. Table 1 presents the results of the many-body Dyson equation calculations of the binding energies of the negative ions of Ba^- $6s^26p_{1/2}$ ($Z = 56$) and Yb^- $4f^{14}6s^26p_{1/2}$ ($Z = 70$), together with the isoelectronic neutral Lu ($Z = 71$). Comparison with the experimental data for Lu and Ba^- shows that when the second-order correlation potential is used, the binding energies are greater than the respective experimental values. The latter are reproduced when $\Sigma^{(2)}$ is multiplied by the scaling factor $\lambda \approx 0.80$ (Lu) and 0.86 (Ba^-). In Yb^- the calculation with $\Sigma^{(2)}$ produces a bound state at -35 meV. When the scaling factor is introduced into the Dyson equation for the $6p_{1/2}$ state, the binding energy shows a linear dependence on λ, see figure 1. This behaviour is typical for all states with orbital momenta $l \geqslant 1$ (see, for example, Baz *et al* 1971).

Table 1. Binding energies of the $6p_{1/2}$ electrons in Lu, Ba^- and Yb^- from experiment and many-body theory calculations.

Atom or ion	Calculation (eV) DF[a]	Calculation (eV) DF+$\Sigma^{(2)}$[b]	Factor λ[c]	Best value (eV)
Lu	4.1847	5.1018	0.8027	4.9131[d]
Ba^-	—	0.2125	0.8592	0.1446[e]
Yb^-	—	0.035	0.83	−0.020[f]

[a] The static Dirac–Fock Hamiltonian of the closed-shell core does not support $p_{1/2}$ bound states when the core is electrically neutral (Ba and Yb).
[b] Dyson equation with the second-order perturbation theory correlation potential.
[c] Factor to multiply the second-order correlation potential.
[d] Experimental value (Radtsig and Smirnov 1986).
[e] The experimental value is 144.62(6) meV (Petrunin *et al* 1995).
[f] Our prediction for the Yb^- $p_{1/2}$ shape resonance.

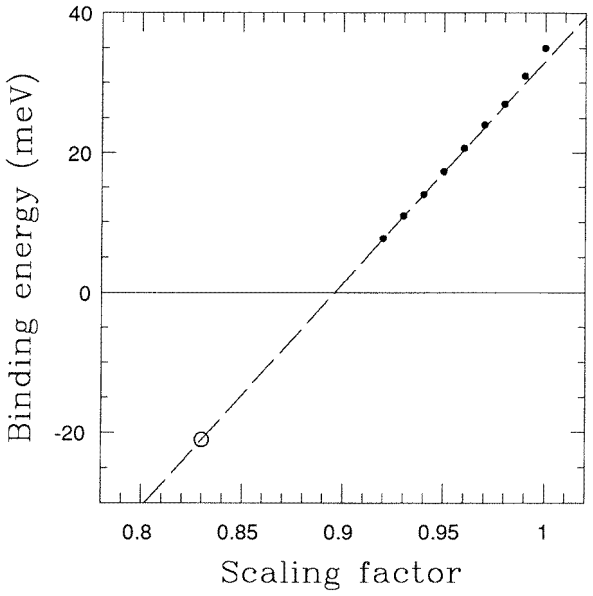

Figure 1. Dependence of the binding energy of the $6p_{1/2}$ electron in Yb^- on the scaling factor λ introduced before the second-order correlation potential: $\Sigma = \lambda\Sigma^{(2)}$. • show the calculated points, — — — is the best linear fit at small binding energies. The expected value of the scaling factor $\lambda \approx 0.83$ suggests that the $p_{1/2}$ state is a resonance in the electron–atom continuum at about 20 meV (○).

At $\lambda \approx 0.90$ the bound state vanishes and becomes a resonance in the continuum. Assuming that the true scaling factor in Yb^- should be somewhere between those of neutral Lu and negative Ba^-, we choose $\lambda = 0.83 \pm 0.03$ as a reliable estimate. This means that the energy of the $p_{1/2}$ state is 20 ± 10 meV *above* the atomic ground state. The other fine-structure component is then also a shape resonance in electron–Yb scattering at about 80 meV (if we use the estimate of the fine-structure interval from Dzuba and Gribakin (1994)).

We believe that we have presented the strongest theoretical evidence obtained so far that atomic Yb cannot form a stable negative ion. This conclusion is in agreement with the recent experimental study by Andersen *et al* (1998). It does not contradict the result of the complex many-body perturbation theory calculations of Avgoustoglou and Beck (1997), if we allow for 10 meV uncertainty in their binding energy value. The most conclusive evidence of the absence of this negative ion would be obtained if the two narrow low-lying shape resonances: $p_{1/2}$ and $p_{3/2}$, around 80 and 20 meV, respectively, were detected in electron scattering from the ground state Yb.

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