Electron affinities and $E1$ f values for 11 bound states of La^- formed by $6p$ and $5d$ attachment

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(Received 22 April 1999)

Relativistic configuration-interaction calculations, including valence and some shallow core-valence correlation indicate that La^- has 11 bound states. The seven odd states arising from 6p attachment have electron affinities (in meV) of 462 ($^1D_2$), 282 ($^3F_2$), 247 ($^3F_3$), 235 ($^3D_1$), 145 ($^3D_2$), 84 ($^3F_4$), and 56 ($^3D_3$). The remaining four bound states are even $5d$ attachments with electron affinities (EA's) of 434 ($^3F_2$), 375 ($^3F_3$), 312 ($^3F_4$), and 62 ($^1D_2$). The majority of these levels are reported here for the first time. Two of these EA's are in good agreement with the recent experimental values of Covington *et al.* [J. Phys. B **31**, L855 (1998)]. The largest $5d$-$6p$ f value is $\sim 0.005\,65$. [S1050-2947(99)00209-7]

PACS number(s): 32.10.Hq, 32.70.Cs, 31.25.Jf, 31.30.Jv

I. INTRODUCTION AND METHODOLOGY

In 1991, Vosko *et al.* [1] put forward the idea that negative ions of rare earths were formed by p and possibly d attachment, and not by the attachment of f electrons, as had been thought previously [2]. The argument was by analogy to the then recent work on Ca^- [3], and supported by a combination of Dirac-Fock and local-density calculations.

Since 1991, further calculations have been done on rare earth negative ions by Vosko *et al.* and Beck *et al.*, using relativistic configuration-interaction (RCI) calculations. These support the idea that formation of the negative ion is mostly by p attachment. A survey may be found in Ref. [4]. Experimentally, many of the rare earth negative ions have been detected, e.g., Litherland and co-workers [5], but few definitive measurements of the electron affinities (EA's) have been made. It appears that a significant experimental difficulty is in formation of the negative ion beam, and as a consequence, Yb^- was chosen to be one of the first ions to be thoroughly studied [6]. Unfortunately, current theory [7] and experiment [6] indicate that if any bound state exists for this species, it's EA is below 10 meV.

La^- was chosen for this paper for several reasons; the general experimental interest in the rare earth negative ions, the relative ''simplicity'' of La^- (no open f subshells), and the ''age'' of the original calculations [1]. In addition, a recent experiment by Covington *et al.* [8], has obtained an electron affinity of 470 meV for La^- and a bound excited state with a binding energy of 170 meV. In fact, La^- is of even more interest, along with Ce^- [9] and Th^- [10], for these are the first negative ions with bound states of both parities, which could permit electric dipole transitions between the negative ion bound states (La^- $E1$ f values $\leqslant 0.005\,65$).

Calculation of attachment energies for d and f electrons is difficult as it requires careful treatment of core-valence correlation, because of ''corelike'' localization of these electrons. As suggested in the work of Vosko *et al.* [1], for example, this can be largely avoided by selecting an appropriate excited state of the neutral atom, to which we can attach an s or p electron. Attachment of such electrons is found to involve less of the core. In La, we attach a $6s$ electron to the $5d^26s$ $J=7/2$ excited state to study $5d$ attachment to the ground state. This $J=7/2$ state is the lowest of its symmetry. Using either the $J=3/2$ or $J=5/2$ $5d^26s$ excited state would mean we would not be dealing with the lowest state, which would be an additional computational complication. In this approach the d attachment core-valence correlation effects are automatically included in the experimental [11] $5d6s^2$-$5d^26s$ energy difference.

Our calculations start by generating a reference function; either a Dirac-Fock (DF) or multiconfiguration Dirac-Fock (MCDF) function obtained using Desclaux's algorithm [12], based on a Dirac-Coulomb Hamiltonian. We next decide what subshells are in the valence space ($5d$, $6s$, and $6p$ here) and what will be in the core (the rest of the subshells). We include all single and double excitations from the valence subshells up to (at least) $l=4$ symmetry. Radial functions not present in the DF (MCDF) solution are represented by relativistic screened hydrogenic functions, whose effective Z (Z^*) is determined during the RCI process. Initial estimates for Z^* are determined by matching the virtual $\langle r\rangle$ to that of the DF/MCDF radial it is replacing.

We next include a limited amount of shallow core-valence correlation; in the present instance, this includes the $5p$ core subshell, specifically $5p$,$6p$ and $5p$,$6s$ pair correlations. These are thought to be the most important core-valence contributions to the EA; they involve the valence subshell whose occupation number is changing (atom to negative ion), and the core subshell whose $\langle r\rangle$ is closest to the valence $\langle r\rangle$, and which has a substantial occupation (six electrons). Exclusion single and double excitations, $5p\rightarrow 6p$ and $5p^2\rightarrow(5d+6s+6p, \mathrm{v}l)$, are also included as they may vary significantly between atom and ion.

Introduction of the core-valence correlation frequently has the effect of reducing (in part, falsely) the near degeneracy (e.g., $6s^2\rightarrow 6p^2$) valence correlation. In the main, what is happening is that there are shallow core-valence pair correlations present in the DF/MCDF solution, not present in the near-degeneracy configurations. When these are restored (and they are frequently triple or quadrupole excitations with respect to the reference function; i.e., they are second-order effects), significant improvements occur in the EA's.

Recent improvements in the RCI methodology, e.g., [13]

TABLE I. Energy contributions to La^- odd-state electron affinities (meV).

Excitation	La I $5d6s^2$ $^2D_{3/2}$	La$^-$ $5d6s^26p$ $^1D_2$	$^3F_2$	$^3F_3$	$^3D_1$	$^3D_2$	$^3F_4$	$^3D_3$
$6p\rightarrow p$	NA[b]	38.0	84.1	39.6	61.6	130.0	27.8	71.0
$6p\rightarrow f$	NA[b]	3.9	2.8	2.5	36.4	34.7	1.7	34.9
$6s\rightarrow d$	156.8	648.0	595.5	556.4	553.2	588.3	567.8	550.3
$6s\rightarrow s+g$	22.1	23.4	16.5	17.5	28.4	29.7	17.0	32.4
$5d\rightarrow s+d+g$	−1.2	11.3	25.1	29.3	1.5	0.0	29.3	0.3
$6s^2\rightarrow p^2$	428.0	282.7	329.7	333.7	308.0	309.9	353.3	322.2
$6s^2\rightarrow d^2$	145.1	147.8	135.6	138.0	143.3	142.5	139.3	135.6
$6s^2\rightarrow s^2+f^2+g^2$	29.0	35.1	34.0	34.1	33.5	33.3	26.8	33.0
$5d\ \ 6s\rightarrow p^2$	75.0	83.9	39.3	21.4	126.0	126.5	23.6	125.7
$5d\ \ 6s\rightarrow pf$	245.2	188.1	213.5	223.7	182.4	178.8	219.2	180.9
$5d\ \ 6s\rightarrow d^2+f^2+g^2+sd+dg$	51.1	6.9	8.8	6.1	14.2	11.2	1.2	11.3
$6s\ \ 6p\rightarrow sp^a+pd+df+fg$	NA[b]	78.6	83.0	100.8	87.7	75.0	77.0	82.6
$5d\ \ 6p\rightarrow sp+pd^a+df^a+fg$	NA[b]	42.2	47.8	50.5	34.2	36.8	50.9	33.6
$5p\rightarrow p$	51.9	39.6	36.1	36.1	62.9	59.6	20.1	59.9
$5p^2\rightarrow p^2$	324.1	310.1	309.9	312.9	311.1	309.6	288.6	296.8
$5p\ \ 6p\rightarrow s^2+p^2+d^2+f^2+g^2+sd+dg+pf$	NA[b]	119.6	122.4	111.7	122.9	127.4	95.7	104.0
Total	1527.1	2138.8	2134.0	2063.4	2150.0	2238.0	1985.6	2116.5

[a]Indicates excitations added to $5d^26s6p$ and $5d6p^3$ where appropriate.
[b]Not applicable.

have relied heavily on increased attention to these second-order effects. Often, during the process of adding correlation and inclusion of extra sets of virtuals, we find certain correlation configurations that exhibit a dramatic loss in their energy contributions. This loss due to ''pulling away'' of nearly degenerate manifolds as the ground-state manifold is more fully correlated can be corrected by several means. The first, which has been explored in detail in this paper is careful tailoring of the DF radial functions to lessen the sensitivity of the calculation on the ''problem'' configurations. For example, in La^- $5d6s^26p$ cases single excitations of the form $6s\rightarrow d$ are found to have a large correlation contribution and exhibit the ''pulling away'' losses. Initial DF radials generated using multiple (nonrelativistic) configurations produced $5d$ radial functions with larger $\langle r\rangle$ than those created using $5d6s^26p$ alone (3.5 vs 3.0 a.u.). Though the difference in DF energy between calculations using either set of radials is only ~ 20 meV (favoring the latter), and the configuration

TABLE II. Energy contributions to La^- even-state electron affinities (meV).

Excitation	La I $5d^26s$ $^4F_{7/2}$	La $^-5d^26s^2$ $^3F_2$	$^3F_3$	$^3F_4$	$^1D_2$
$6s\rightarrow d^a$	3.9	56.5	55.5	57.9	184.0
$6s\rightarrow s^a+g^a$	14.5	65.6	70.1	68.1	30.1
$5d\rightarrow s+d+g$	14.6	15.5	12.4	12.9	160.1
$6s^2\rightarrow p^2$	NA[b]	349.1	348.9	347.1	348.1
$6s^2\rightarrow s^2+d^2+f^2+g^2$	NA[b]	105.5	108.4	109.0	101.7
$5d\ \ 6s\rightarrow p^{2\,a}$	6.4	225.3	226.7	225.7	188.4
$5d\ \ 6s\rightarrow sd^a$	53.5	125.5	127.4	129.2	131.8
$5d\ \ 6s\rightarrow pf^a$	205.2	332.6	336.0	339.8	327.5
$5d\ \ 6s\rightarrow d^2+f^2+g^2+dg$	9.8	27.4	27.9	28.5	18.1
$5d^2\rightarrow d^2$	39.3	44.9	44.2	44.4	67.9
$5d^2\rightarrow f^2$	71.7	67.5	65.0	64.6	148.8
$5d^2\rightarrow p^2+g^2+sd+dg+pf$	36.11	32.3	30.4	31.1	103.1
$5p\ \ 6s\rightarrow sp+pd+df+fg$	450.4	540.6	543.6	546.5	537.0
$5p\ \ 5d\rightarrow sp+sf$	81.9	65.2	63.9	62.4	64.9
$5p^2\rightarrow s^2+sd$	61.0	38.6	39.2	39.5	37.0
Total	1048.2	2092.2	2096.4	2108.6	2435.0

[a]Indicates excitations added to $5d^2\ vp^2$, $5d\ 6s\ vp^2$, $5d\ 6s\ vp\ vf$, and $5d\ 6s\ vs\ vd$, where appropriate.
[b]Not applicable.

TABLE III. Electron affinities (meV) and *LS* composition for La^- bound states.

This work (RCI)		Vosko *et al.* [1]		Covington *et al.* [8]
$5d\ 6s^2 6pJ=2$ (76.8% ^{1}D, 20.7% ^{3}F, 1.3% ^{3}P, 1.2% ^{3}D)	462	$^1D^o$	270–410	470
$5d\ 6s^2 6pJ=2$ (77.6% ^{3}F, 20.9% ^{1}D, 0.8% ^{3}P, 0.7% ^{3}D)	282	$^3F^o$	110–220	
$5d\ 6s^2 6pJ=3$ (99.2% ^{3}F, 0.7% ^{3}D, 0.1% ^{1}F)	247			
$5d\ 6s^2 6pJ=1$ (99.4% ^{3}D, 0.5% ^{1}P, 0.1% ^{3}P)	235	$^3D^o$	140–220	
$5d\ 6s^2 6pJ=2$ (96.6% ^{3}D, 1.8% ^{3}P, 1.3% ^{3}F, 0.3% ^{1}D)	145			170
$5d\ 6s^2 6pJ=4$ (100.0% ^{3}F)	84			
$5d\ 6s^2 6pJ=3$ (96.5% ^{3}D, 2.9% ^{1}F, 0.6% ^{3}F)	56			
$5d^2\ 6s^2 J=2$ (97.5% ^{3}F, 2.4% ^{1}D, 0.1% ^{3}P)	434	$^3F^e$	110–270	
$5d^2\ 6s^2 J=3$ (100.0% ^{3}F)	375			
$5d^2\ 6s^2 J=4$ (99.7% ^{3}F, 0.3% ^{1}G)	312			
$5d^2\ 6s^2 J=2$ (88.4% ^{1}D, 9.0% ^{3}P, 2.6% ^{3}F)	62			

interaction (CI) energy is minimally (a few meV) affected in smaller calculations, the effect is to lessen the overall importance of the $6s \rightarrow d$ configurations (and hence the ''pulling away'' problem) by ~ 80 meV in the larger final runs. Secondly, we may obtain a similar improvement by also tailoring the initial set of virtual orbitals toward the larger contributing (to the EA) and ''problem'' configurations. Iterating Z^* for the first set of virtuals using a limited calculation containing only the most important valence configurations aids in the saturation of these configurations as further virtuals are added. This careful choice of Z^* is helpful in the final step in correcting losses of ''problem'' configurations by inclusion of purely second-order effects. By careful selection of excitations, which are important in the manifold(s) of interest and application of these excitations to the ''problem'' configurations, we account for a significant portion of the ''pulling away'' of these nearby manifolds. Maximizing the effect of the first set of virtuals as described above generally ensures that we need only deal with the primary set of virtuals when including these triple and/or quadruple excitations. For further discussion of second-order effects, see Sec. I of Ref. [13].

II. RESULTS

Energy contributions to odd and even bound state EA's of La^- are summarized in Tables I and II, respectively. The entries in these tables represent a summation over contributions of three sets of virtual orbitals (vl, vl', and vl''), as well as a fourth vp in the odd cases. The first two sets are fully included, and the third set (and fourth vp) are added to configurations in which the second set of virtuals contributes significantly (i.e., those that are not sufficiently saturated with inclusion of the second set). In addition, we collect contributions of excitations of the same symmetry and, in some cases, of the same type for those configurations with relatively minor contributions to the energies.

In La^- we identify several ''problem'' configurations as discussed in the last section. For the $6p$ attachment these are $6s \rightarrow 5d$ and $6s^2 \rightarrow 6p^2$. In the even $6s$ attachment we see significant losses to $6s^2 \rightarrow vp^2$ and $5d6s \rightarrow vp^2 + vp\ vf$ as well as moderate loss in $5d\ 6s \rightarrow vs\ vd$. In both cases the majority of second-order improvements result from the lessening of the restriction on J for pair excitations from the $6s^2$ subgroup (allowing $J>0$). Additional second-order effects are indicated in Tables I and II. An estimate for the overall contribution of second-order effects presented here and in the previous section is to increase the binding of the negative ion by as much as 100 meV.

In Table III we present our values for the EA's of the eleven bound states of La^-. The *LS* composition (DF level) of our levels agrees with the ordering predicted by Vosko *et al.* [1], but the electron affinities themselves better agree with the larger experimental values given by Covington *et al.* [8]. Current estimates for errors of our RCI EA's are approximately 30 meV, perhaps larger for the higher excited states as our calculations are optimized to the lowest level of a given J and parity. Note that for even moderate errors the relative positioning of the many levels of this rich system may be disturbed. In particular, given the difference of less than 30 meV between the $^1D_2^o$ and $^3F_2^e$ levels, the parity of the La^- ground state is not definitively predicted by this paper. An indication as to the importance of correlation in relative positioning of levels with respect to those of the same parity can be inferred by the differences of the total correlation contribution (in some cases, greater than 100

TABLE IV. La^- *LS* allowed transition f values.

Transition	f value (length)
$^1D_2^o \rightarrow {}^1D_2^e$	1.30×10^{-3}
$^3F_2^e \rightarrow {}^3F_2^o$	5.41×10^{-4}
$\rightarrow {}^3F_3^o$	1.11×10^{-4}
$\rightarrow {}^3D_1^o$	3.30×10^{-3}
$\rightarrow {}^3D_2^o$	5.17×10^{-4}
$\rightarrow {}^3D_3^o$	3.97×10^{-6}
$^3F_3^e \rightarrow {}^3F_2^o$	2.76×10^{-5}
$\rightarrow {}^3F_3^o$	6.48×10^{-4}
$\rightarrow {}^3D_2^o$	4.50×10^{-3}
$\rightarrow {}^3F_4^o$	1.10×10^{-4}
$\rightarrow {}^3D_3^o$	3.78×10^{-4}
$^3F_4^e \rightarrow {}^3F_3^o$	1.12×10^{-5}
$\rightarrow {}^3F_4^o$	1.36×10^{-3}
$\rightarrow {}^3D_3^o$	5.65×10^{-3}

meV) given at the bottom of Tables I and II.

Finally, in Table IV we present electric dipole f values for LS allowed transitions of La^-. It would be interesting to have these weak $E1$ f values measured in the future—to our knowledge, no such $E1$ transition between stable negative ion states has been observed yet. We present values calculated using the length gauge only. The small energy differences involved here make accurate velocity gauge calculations difficult to obtain.

ACKNOWLEDGMENT

Support from the National Science Foundation under Grant No. 96-05213 is gratefully acknowledged.

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