

Relativistic configuration interaction calculations of electron affinities for 3 bound states of Lu^- formed by 6p attachment

Steven M O'Malley and Donald R Beck

Physics Department, Michigan Technological University, Houghton, MI 49931, USA

Abstract.

Valence shell relativistic configuration interaction calculations indicate three bound states for Lu^- by $6p$ attachment to the $5d\ 6s^2\ J = 3/2$ ground state. These include two $J = 2$ levels with electron affinities of 329 and 124 meV, as well as one $J = 3$ level at 63 meV. The first value is 139 meV larger than the previously published value, while the latter two are predicted here for the first time. We find second order effects moderately important in the binding of these states, while certain core excitations (particularly involving the 4f subshell) were found to have a negligible impact.

PACS numbers: PACS numbers: 32.10.Hq, 31.25.Eb, 31.25.Jf

Short title: RCI electron affinities of Lu^-

July 20, 2000

1. Introduction

Electron affinities of the rare earths are the least well known [1] of any group of atoms in the periodic table. Experimentally, with the exception of La^- [2], their anions have been detected for most species [3], but not further characterized. Early theoretical treatment, e.g. [4], using local density methods, predicted fairly high EAs, arising from attachment of f electrons. More modern work, starting with that of Vosko *et al* [5] has focused on p attachment (and sometimes *d* attachment) to form the anion, and results have been produced for the “edges” of the lanthanide row [5, 6, 7, 8, 9, 10] La, Ce, Pr, Tm, Yb and Lu and the actinide row, *viz.* Ac, Th, Pa and U [11, 12, 13, 14]. It is well recognized that both correlation and relativistic effects must be included, if reliable EAs are to be produced. The inclusion of an adequate amount of correlation is greatly complicated by the presence of open shell f electrons characteristic of these species, and this has been one primary reason for the absence of modern calculations for the EAs in the middle of these two rows.

The first measurement of EAs for the Lanthanides has been done for La^- itself by Thompson *et al* [2]. Two bound states were found with EAs substantially (~ 100 meV) greater than those predicted by Vosko [5]. Prior to the appearance of the experimental work, we had undertaken a calculation of the La EAs, with a careful accounting of second order correlation effects, which we had just begun to systematically include [15]. Inclusion of second order effects increased EAs by ~ 100 meV, yielding results consistent with experimental values, and predicting [16] 11 bound states for La^- in contrast with the earlier Vosko [5] work which had 4. Further experimental and theoretical work is needed for La^- before the 6p attachment process can be confirmed.

Since further experimental work on the lanthanides seems likely in the near future, we have redone our calculation for the EAs of Ce^- [17], including the important second order effects. This increased the EAs over those of Dinov *et al* [6] ~ 100 meV and led to a prediction that there were 15 bound states instead of the 6 previously reported. In this work, we apply our methodology to Lu^- for which there currently exists only the older Vosko EAs [9] with the finding that there are likely 3 not 1 bound states, and with an increase of the Vosko value for the EA of ~ 100 meV.

2. Methodology

Wavefunctions are calculated using the Relativistic Configuration Interaction (RCI) method, the details of which can be found in a series of papers [18] and references therein. We begin with a Dirac-Coulomb or Dirac-Breit Hamiltonian, and a zeroth order, or reference function, is generated by solving Multiconfigurational Dirac-Fock (MCDF) equations using a modified version of Desclaux’s program [19]. The most

important modifications are to allow up to 1000 eigenvectors, 1 million “extra” R^k integrals (the number of unique R^k integrals is more than 10 times smaller), and non-integer Z s. The first two are necessary because of great complexity of the rare earth states due to the open f shell electrons, and the last, because one often must generate negative ion MCDF radials by “stepping” down isoelectronically from higher Z ’s, in charge decrements as small as 0.05. In the case of Lu^- , with the 4f shell full, the size of the MCDF calculation is more modest with 14(12) eigenvectors and 151(130) extra R^k integrals (total R^k integrals $\sim 58\,000$) for $J = 2(3)$.

Once the MCDF reference (i.e. dominant) manifold is generated, first order perturbation theory is formally applied (with the Coulomb operator as the normal perturbation) to generate the form for the correlated “first order” wavefunction. This function is constituted by single and double subshell excitation from the reference. The amount of excitation from the core is determined by practicability, and past experience. In the present instance of Lu^- , excitations from the closed 4f subshell were allowed, but found to be negligible (see next section).

Generally, single and double excitation occurs into subshells not occupied in the MCDF reference, and radial functions need to be generated for these “virtual” subshells (denoted $v\ell$). As has been recognized by most CI practitioners since the 1960’s [20] these virtual radials are not “spectroscopic”, but rather represent the compact portions of infinite Rydberg/continuum series (for bound states), when obtained within the CI (RCI) process. Our long standing preference has been to use a few analytic functions to represent each virtual radial, which allows their easy adjustment (change of one parameter, called the effective charge, or Z^*), after which they are converted to the numerical mesh of Desclaux [19] to improve computational efficiency. For the RCI methodology, we have found use of a relativistic screened (Z^*) hydrogenic function (SHF) an excellent choice. It is capable of acquiring about 90% of the correlation energy, while avoiding variational collapse into the positron sea as a result of the simultaneous choice of both major and minor components, once Z^* is fixed. As is typical of single particle expansions, convergence is slow after 1 SHF, but in practice, we find that no more than 3 SHF are need per virtual radial, for each reference shell being excited. Good estimates for the initial Z^* s can be obtained by equating each $\langle r \rangle$ for the shell being excited, and its virtual replacement.

A “first order” correlation configuration can involve thousand of eigenvectors of the desired J and M_J , and in the interests of computational efficiency, interpretability and usability of the final wavefunction, we would prefer to keep our CI sizes as small as possible (7000 currently, to be increased to 20 000 soon). This can be achieved, with little error (50-200 cm^{-1}), with the following “first order” concept based on the idea of Bunge [21], which we call REDUCE [22]. First, the matrix elements $\langle \phi | H | X \rangle$ are constructed in the original basis. Here ϕ is the MCDF eigenvector, X is any of the

n eigenvectors for the correlation manifold we wish to REDUCE, and H is the Dirac-Coulomb Hamiltonian (Breit effects are small for EAs, and may be obtained after the RCI wavefunction has been created or during the MCDF stage). Each of the n matrix elements can be written as a linear combination of m radial integrals (one and two particle), and for most every case $m \ll n$. To take advantage of this, the original “ X ” basis is rotated to a “ Y ” basis, chosen to maximize the number of zero matrix elements. Those members of the Y basis yielding zero matrix elements are then discarded, reducing to basis size from n to m - a reduction which could be of as much as a factor of 1000, and which is greater, the more complicated the X manifold is. These largest reductions are achieved by ignoring the j dependence of radial integrals when performing the reduction, thus lowering m . As an example, $F^0(6s_{1/2}, 6p_{1/2})$ and $F^0(6s_{1/2}, 6p_{3/2})$ would be treated as the same integral (this option may be disengaged, if necessary). As stated earlier, tests have shown that errors are in the 50-200 cm^{-1} range, smaller than other errors arising from missing configurations, for example.

However, for our most recent work [16, 15, 23] use of just a “first order” RCI wavefunction has proven to be inadequate. What has been observed is that the energy contribution of nearly degenerate excitations decrease as the MCDF reference function is correlated (in our methodology, we proceed in layers, working from the outer towards the inner shells). We ascribe this to the “pulling away” of the MCDF manifold from these problem configurations, because we are adding correlation to the former, but not the equivalent correlation to the latter. Crudely speaking, this lowers the energy contribution by changing the energy difference between the MCDF and correlation diagonal matrix elements. It is “repaired” by correlating these excitations in the analogous way that the MCDF manifold was correlated. This often corresponds to inclusion of triple and quadruple excitation, as well as double excitations with zero first order interaction with the manifold of interest, i.e. inclusion of second order effects. For example, in our recent study of Ce^- [17], we found that for the $4f 5d^2 6s^2$ states the configurations $4f 5d 6s vp^2$ ($5d 6s \rightarrow vp^2$) and $4f 5d 6s vp vf$ ($5d 6s \rightarrow vp vf$) exhibited significant losses (on the order of 20 meV) in their total contributions (> 200 meV each) between smaller test runs and the fully correlated calculation. We add some correlation to these problem configurations by simply removing the first order $1 \leq J \leq 3$ restriction on all $5d 6s$ pair excitations (vp^2 can make $J = 0$ and $vp vf$ can make $J = 4$). We also add explicitly second order effects in the form of some quadruple excitations derived from applying excitations important in the $4f 5d^2 6s^2$ manifold to these configurations, including $5d 6s \rightarrow vp^2$ and $5d 6s \rightarrow vp vf$ themselves, i.e. the quadruples (with respect to $4f 5d^2 6s^2$) $5d^2 6s^2 \rightarrow vp^4 + vp^3 vf + vp^2 vf^2$. For EAs, these have been found to be as large as 100 meV in La^- [16] and Ce^- [17] (with $\sim 1/3$ of the correction resulting from inclusion of triples and quadruples), while they have had a more moderate effect in the case of Lu^- (see next section).

3. Calculations and results

As mentioned previously, our calculations begin by generating MCDF reference functions using Desclaux's program [19]. From past experience [16, 17] we prefer to create MCDF radials using a single manifold ($5d\ 6s^2\ 6p$ for Lu^- and $5d\ 6s^2$ for the Lu I threshold). Though radials produced using several configurations, result in a somewhat lower MCDF energy (typically on the order of 20 meV), we find that the single configuration radials are more similar between the neutral and negative species (as indicated by comparison of $\langle r \rangle$ of individual subshells). This similarity is most important here for the $5d$ subshell (which is more core-like than the $6s$ or $6p$). The more alike the two $5d$ radials are, the less disparity we find in energy contributions for excitations involving $5d$. This is important because we would like to avoid opening the shallow core as this would introduce 1 eV or more extra correlation, compounding the pulling away losses discussed in the prior section. Minimization of the differential importance of, for example, $4f\ 5d$ pair excitations is thus essential. For Lu^- $J = 3$, however, the code [19] does not converge with a single nonrelativistic configuration. Fortunately, we are able to obtain a solution by including $6s^2 \rightarrow 6p^2$, which affects the $5d$ radial only minimally (by comparison with the two $J = 2$ cases for which the single configuration calculation does converge). For consistency, we then treat all 4 sets of radial calculations (the neutral, $J = 3$, the lower $J = 2$, and a separate $J = 2$ optimized to the excited state) as two configuration calculations.

As a result of our careful choice of radial bases, sample runs comparing $4f\ 5d$ pair excitations between Lu I and the Lu^- $J = 2$ ground state indicate a differential energy contribution of 10 meV. A larger test run including single excitations from $5s$, $5p$, and $4f$ as well as $5s\ 6p$, $5p\ 6p$, and $4f\ 6p$ pair excitations (particularly those with one or two electrons into the $5d$ subshell) indicate that effects of these two groups of configuration cancel each other to within a few meV (the single excitations unbind the system due to a differential contribution of ~ 100 meV, while the pair excitations involving $6p$ are not present in Lu I and attribute nearly the same amount of correlation in the opposite direction). Likewise, exploration of the $4f^2$ and $5p^2$ excitations that would be required if we opened these subshells shows an increase the EAs of ~ 30 meV (considering first order contributions only). Though not insignificant, such energy differences do not warrant opening of the shallow core for two reasons. First, inclusion of these excitations in the larger RCI calculation would increase the total energy contribution due to correlation to 3 eV or more (considering only, for example, the exclusion effects $4f^2 \rightarrow 5d^2 + 5d\ v\ell$ - inclusion of $4f^2 \rightarrow v\ell\ v\ell'$ may add 10 eV or more). This likely would introduce second order losses due to "pulling away" of the $5d\ 6s^2\ 6p$ manifold on the order of hundreds of meV, larger than the contribution of most of the individual valence excitations (see table 1). In fact, the test runs mentioned above showed second order losses in

energy contribution of valence configurations that were several times the difference in the contributions due to inclusion of core excitations. The efforts required to recover second order losses of this magnitude would quickly exhaust our limits on the RCI basis (possibly even with an increase to 20 000 basis members). The second consideration is that the test runs on core excitations typically involve a single set of virtual orbitals (or two in the case of the less complex case involving single excitations and $n\ell$ 6p pair excitations). Saturation of these configurations through inclusion of further sets would likely change these contributions by tens of meV (though not necessarily the differences). In any case, we regard the difference in energy contribution of core effects on the order of a few percent of their total contribution as negligible in comparison with the benefits of proceeding with a valence shell only RCI calculation. Simply put, it is the relative independence of the Lu^- EAs on core excitations that allows us to proceed with these calculations at this time, though we will certainly need to expand our methods to deal with future cases with open f shells where the dependence on core excitations is not so minor.

We include all single and double excitations from the valence orbitals with virtual orbitals ($v\ell$) up to $\ell = 4$. For the first set of virtual orbitals (for which we expect to account for about 90% of the correlation contribution for each configuration) we make comparisons to smaller runs involving only a few important configurations to identify the “problem” configurations that require further correlation. Second order effects are then included as described in the previous section at this stage. The second set of virtual orbitals is included in all of the first order configurations, as well as those resulting from removal of J restrictions on pair excitations, e.g. $6s^2 \rightarrow vs vd$. Those configurations for which inclusion of the second set of virtuals that contribute less than 1 meV to correlation energies in each of the Lu^- and Lu I levels are considered saturated. A third set added to the remaining configurations is found to be sufficient to saturate them. Final runs for the Lu^- $J = 2$ and $J = 3$ levels contain 6388 and 6638 parents, respectively, with CPU times on a 500 MHz Alpha Station of about 30 minutes (run times can approach 90 minutes at intermediate stages, depending on the number of virtuals being iterated and initial choices for Z^*s).

Energy contributions from correlation configurations are given in table 1. These are computed using the intermediate normalization $\langle \Phi | \Psi \rangle = 1$ from

$$\Delta E(i) = \frac{c_i}{c_0} \langle \Phi | H | \chi_i \rangle \quad (1)$$

where Φ is the reference function, c_0 is the RCI coefficient of Φ , χ_i is a correlation function, and c_i is the RCI coefficient of χ_i . Also noted in table 1 are the problem configurations and the excitations added to them as second order effects. The EAs are given in table 2 along with the LS percentages, which are computed at the Dirac-Fock level. LS composition is determined by diagonalizing the $L^2 + S^2$ matrices with the

assumption that the minor components are negligible and the major (radial) components are independent of j . The RCI reference is then decomposed in this basis. Also for reference in table 2 is the EA estimate from Vosko *et al* [9]. Though the error bars on that estimate are quite large, we do note that the difference between our calculation and that of the Vosko group is ~ 140 meV, roughly the same range as our differences in the case of La^- (~ 120 meV) [16, 5] and Ce^- (~ 90 meV) [17, 5]. In these two cases we have attributed our differences from the older EAs to inclusion of second order effects. In this case, however, we find a more moderate effect on the difference due to second order effects. In the case of Lu^- , second order effects were found to be roughly half as important as indicated by the column Δ_{20} in table 2. This reduction of the importance of second order effects is primarily due to cancellation from a 48 meV difference in the neutral energies with and without second order configurations, whereas in La^- [16] and Ce^- [17] second order effects were found to be negligible in the neutral threshold. This disparity is due to the importance of the $6s^2 \rightarrow vp^2$ excitation in the Lu I ground state (see table 1) and the relaxation of the J restriction (>0) on the vp^2 subgroup and all other $6s^2$ pair excitations. (The neutral thresholds in the other two cases contain a $5d^2 6s$ subgroup rather than the corresponding $5d 6s^2$ configuration here).

Finally, we report a possible candidate for an opposite parity bound state. These are interesting because they are relatively rare (recently observed in Os^- [24] and predicted for La^- [5], Ce^- [6], Th^- [12] and Ac^- [11]) and might be observed via E1 transitions. Separate valence calculations made by 6p attachment to the excited Lu I $6s^2 6p J = 1/2$ state (at 512.8 meV [25]), indicate a potential bound $6s^2 6p^2 J = 0$ level with EA = 33 meV. However, considering that our stated goal in recent calculations is to acquire energies accurate to ~ 30 meV (based upon comparison between prior calculations [15] and experimental values where they are available [26]), this finding is inconclusive.

Acknowledgments

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

References

- [1] Andersen T, Haugen H K and Hotop H 1999 *J. Phys. Chem. Ref. Data* **28** 1511
- [2] Covington A M, Calabresse D, Thompson J S and Kvale T J 1998 *J. Phys. B* **31** L855
- [3] Nadeau M J, Garwan M A, Zhao X L and Litherland A E 1997 *Nuc. Inst. Meth. B* **123** 521 [The lead author in references 31, 33, and 34 of this work should be Dinov (not Dimov).]
- [4] Guo Y and Whitehead M A 1989 *Phys. Rev. A* **40** 28
- [5] Vosko S H, Lagowski J B, Mayer I L and Chevary J A 1991 *Phys. Rev. A* **43** 6389
- [6] Dinov K, Beck D R and Datta D 1994 *Phys. Rev. A* **50** 1144
- [7] Dinov K D and Beck D R 1995 *Phys. Rev. A* **51** 1680
- [8] Chevary J A and Vosko S H 1994 *J. Phys. B* **27** 657
- [9] Vosko S H and Chevary J A 1993 *J. Phys. B* **26** 873
- [10] Avgoustoglou E N and Beck D R 1997 *Phys. Rev. A* **55** 4143
- [11] Vosko S H and Chevary J A 1993 *J. Phys. B* **26** 873
- [12] Datta D and Beck D R 1994 *Phys. Rev. A* **50** 1107
- [13] Dinov K D and Beck D R 1996 *Phys. Rev. A* **53** 4031
- [14] Dinov K D and Beck D R 1995 *Phys. Rev. A* **52** 2632
- [15] O'Malley S M and Beck D R 1998 *Phys. Rev. A* **57** 1743
- [16] O'Malley S M and Beck D R 1999 *Phys. Rev. A* **60** 2558
- [17] O'Malley S M and Beck D R 2000 *Phys. Rev. A* **61** 034501
- [18] Beck D R 1988 *Phys. Rev. A* **37** 1847
- [19] Desclaux J P 1975 *Comp. Phys. Commun.* **9** 31
- [20] Oksuz I and Sinanoglu O 1969 *Phys. Rev.* **181** 42
- [21] Bunge A 1970 *J. Chem. Phys.* **53** 20
- [22] Beck D R and Datta D 1993 *Phys. Rev. A* **48** 182
- [23] Norquist P L, Beck D R, Bilodeau R C, Scheer M, Srawley R A and Haugen H K 1999 *Phys. Rev. A* **59** 1896
- [24] Bilodeau R C and Haugen H K 2000 *Phys. Rev. Lett.* **85** 534
- [25] Martin W C, Zalubas B and Hagan L 1978 *Atomic Energy Levels, The Rare Earth Elements NSRDS-NBS60* (Washington DC: US GPO) p. 401
- [26] Scheer M, Bilodeau R C, Brodie C A and Haugen H K 1998 *Phys. Rev. A* **43** 1357

Tables and table captions

Table 1. Energy contributions (-meV) to Lu^- 5d 6s² 6p EAs.

Excitation	Lu I		Lu ⁻	
	$J = 3/2$	$J = 2$ (ground)	$J = 2$ (excited)	$J = 3$
6p \rightarrow p	—	79.1	57.0	43.7
6s \rightarrow s+g	33.9	35.8	34.2	32.1
6s \rightarrow d ^{a,b}	93.0	475.0	416.9	349.0
5d \rightarrow s+d+g ^a	0.3	4.5	30.8	7.7
6s 6p \rightarrow sp ^a +pd ^a +df ^a +fg	—	140.1	160.5	169.8
6s ² \rightarrow s ² +f ² +g ²	36.7	40.9	42.6	41.8
6s ² \rightarrow p ² ^b	548.3	388.0	391.0	402.1
6s ² \rightarrow d ² ^b	109.5	129.9	121.8	119.9
5d 6p \rightarrow sp+pd ^a +df+fg	—	67.5	59.4	68.5
5d 6s \rightarrow d ² +f ² +g ² +dg	10.6	6.7	9.6	10.7
5d 6s \rightarrow p ² ^b	196.9	153.0	100.6	58.5
5d 6s \rightarrow sd ^a	80.2	97.2	100.3	105.6
5d 6s \rightarrow pf ^b	233.0	206.6	218.9	232.0
Total CI (-meV)	1342.2	1824.1	1743.8	1641.3
MCDF Energy (a.u.)	-14572.5341856	-14572.5285523	-14572.5239847	-14572.5255128
RCI Energy (a.u.)	-14572.5835143	-14572.5955898	-14572.5880703	-14572.5858342

^a Indicates excitations added to problem configurations where applicable. ^b Indicates problem configurations.

Table 2. Electron affinities (meV) and LS composition for Lu^- 5d 6s² 6p bound states. LS % is from calculation of approximate LS states at the MCDF level. Δ_{2O} indicates effect of second order effects on EA (meV).

	5d 6s ² 6p Levels	RCI EA	Δ_{2O}	Vosko <i>et al</i> [9]
$J = 2$	54% ¹ D 43% ³ F 2% ³ P 1% ³ D	329	58	¹ D ₂ + ³ F ₂ 190 \pm 110 meV
$J = 2$	71% ³ F 27% ¹ D 1% ³ P 1% ³ D	124	39	
$J = 3$	99% ³ F 1% ¹ F	63	41	