Electron affinities and $E1$ f values for 15 bound states of Ce^- formed by $6p$ and $5d$ attachment

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(Received 6 October 1999; published 10 February 2000)

Valence shell relativistic configuration interaction calculations yield 15 bound states for Ce^-. These include eight $6p$ attachments calculated with respect to the $4f5d6s^2$ $J=4$ ground state with the following electron affinities (in meV with corresponding J in parentheses): 349 (9/2), 215 (7/2), 203 (5/2), 153 (7/2), 135 (3/2), 117 (11/2), 104 (9/2), and 53 (7/2). The remaining seven bound states are $5d$ attachments, treated as $6s$ attachments with respect to the excited $4f5d^26sJ=8$ threshold, with the following electron affinities: 428 (7/2), 327 (9/2), 281 (9/2), 193 (11/2), 182 (7/2), 167 (9/2), and 149 (11/2). Core-valence effects were found to be minimal, and improvements with respect to our earlier work [K. Dinov, D. R. Beck, and D. Datta, Phys. Rev. A **50**, 1144 (1994)] have been ascribed to better treatment of second order effects (in the case of the $6p$ attachments) and a more appropriate choice of neutral threshold (in the case of the $5d$ attachments).

PACS number(s): 32.10.Hq, 31.25.Jf, 32.10.Fn, 31.15.−p

I. INTRODUCTION

In 1991, Vosko *et al.* [1] suggested that negative ions of rare earths were formed by p and perhaps d attachments, rather than the previously expected f attachment. This argument was supported by the then recent Ca^- work [2]. Systems such as La^- and Ce^- are excellent candidates for exploration of these multiple attachment mechanisms due to the richness of the spectrum of low lying excited states in the neutral species. In 1994, Dinov *et al.* [3] predicted opposite parity bound states in Ce^- with an odd state electron affinity (EA) of 178 meV and 5 even state EA's, the largest being 259 meV. Recent resurgence in experimental interest in rare earth negative ions, e.g., La^- [4], as well as our own recent work on La^- [5], have encouraged us to investigate possible improvements in our older Ce^- calculations.

There are two main improvements in our method that have been implemented in recent years that are expected to affect the Ce^- calculations. The first is an increasing use of second order effects, which has been seen to affect positioning within manifolds (Sn^- [6]) and binding of negative ions with respect to their neutral thresholds (La^- [5]) by as much as 50–100 meV. We introduce second order effects as a means of accounting for the extra correlation of our manifolds of interest with respect to nearby important configurations. Often, as our calculations progress we see a marked loss in correlation energy contribution from problem configurations. Here ''nearby'' configurations are typically identified as those with weights (sum of squared coefficients) of over 1%. Since the RCI coefficients are inversely proportional to differences in diagonal matrix elements of the Hamiltonian, the ''nearby'' configurations (for which the extra correlation is a larger percent of the energy difference) suffer most. We can recoup some of these losses by adding configurations which represent the same types of excitations to the problem configurations as are present in our manifolds of interest. In general, these extra correlation configurations take the form of second order effects (triple or quadruple excitations) with respect to the configuration of interest. Though inclusion of second order effects is limited by our basis set size (7000 parents maximum), recent work [5,6] has expanded use of these effects to as much as 1/3 of the basis members.

The second major improvement made here over the earlier work is in the choice of threshold for the $5d$ attachment. The corelike nature of the $5d$ subshell requires careful treatment of core-valence effects, specifically $5p$,$5d$ pair excitations. Instead we treat the process as an attachment to a $4f5d^26s$ excited state via a $6s$ electron. The benefit is illustrated by the odd $J=7/2$ case where we have $5p$ and $5d\langle r\rangle=\sim 1.8$ a.u. and ~ 3.0 a.u., respectively, whereas the more diffuse $6s$ orbital has $\langle r\rangle=\sim 6.6$ a.u. Though the original paper [3] did treat the problem as a $6s$ attachment, the threshold was chosen as the $4f5d^26sJ=3$ level (293.4 meV [7] above the $J=4$ ground state), which had considerable problems with mixing in the neutral calculation with the lower $4f5d6s^2$ $J=3$ (at 206.2 meV [7]) as well as nearby higher $4f5d^26sJ=3$ levels. In this work we alleviate this problem by chosing the threshold as $4f5d^26sJ=8$ (844.3 meV [7]), which has no corresponding $4f5d6s^2$ levels (or nearby higher $4f5d^26s$ as in the $J=7$ case at 659.1 meV [7]) with which to mix.

II. METHODOLOGY

Our calculations begin by generating either Dirac-Fock (DF) or multiconfigurational Dirac-Fock (MCDF) reference functions using Desclaux's program [8]. The choice for the $5d/6s$ attachment threshold also dictates our choice of radial functions. Since we have the same $5d$ occupation in both the negative ion and the neutral, we would like the corresponding $5d$ radial functions to be as ''similar'' as possible, using $\langle r\rangle$ again as an indicator. The choice of MCDF radials, created with the inclusion of $4f5d^36s$ and $4f5d^4$, does give a slightly lower DF energy (by ~ 20 meV), but the $5d$ radials produced from a single configuration ($4f5d^26s^2$) are much closer to those of the neutral (specifically, the $5d_{5/2}\langle r\rangle$ is $\sim$ 0.3 a.u. larger in the MCDF calculation). Whereas the 20 meV is ''made up'' as we saturate our basis using the single configuration radials, we would possibly have a mismatch due to neglecting core-valence effects involving $5d$ were we to use the MCDF radials.

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TABLE I. Energy contributions to Ce^- even state ($6p$ attachment) electron affinities ($-$meV).

	Ce I $4f5d6s^2$	Ce^- $4f5d6s^26p$							
Excitation	$^1G^o_4$	$^2H^e_{9/2}$	$^2G^e_{7/2}$	$^4G^e_{5/2}$	$^4H^e_{7/2}$	$^2D^e_{3/2}$	$^2H^e_{11/2}$	$^4I^e_{9/2}$	$^2F^e_{7/2}$
$6p\rightarrow p^a+f$	NA[c]	21.9	65.7	53.5	61.7	33.6	65.5	127.6	61.5
$6s\rightarrow d^{a,b}$	142.8	645.2	632.8	624.4	635.6	574.0	620.9	648.8	603.4
$6s\rightarrow s+g$	28.7	27.2	34.9	29.7	33.9	31.6	24.3	26.5	35.8
$5d\rightarrow d^a$	107.2	95.9	182.9	99.7	114.8	92.1	93.5	179.1	277.3
$6s6p\rightarrow sp+pd+df$	NA[c]	73.4	65.8	69.4	72.3	73.7	74.2	69.7	69.8
$6s^2\rightarrow s^2$	14.7	18.8	19.8	19.0	19.9	18.8	19.7	18.5	19.6
$6s^2\rightarrow p^{2\ b}$	469.2	346.7	358.5	355.3	344.9	357.5	356.7	364.1	347.8
$6s^2\rightarrow d^2$	139.2	151.5	139.8	148.7	147.3	147.1	140.3	139.9	141.9
$5d6p\rightarrow pd+df$	NA[c]	48.7	45.4	44.4	36.1	43.6	56.8	57.4	42.5
$5d6s\rightarrow p^2$	88.8	74.6	97.2	89.0	110.0	94.0	48.4	48.9	110.9
$5d6s\rightarrow sd^a$	44.0	55.7	54.0	57.1	53.4	55.7	57.2	56.4	52.8
$5d6s\rightarrow pf^a$	166.4	146.0	136.4	147.7	132.5	142.3	153.7	156.2	134.0
Total	1201.0	1704.3	1833.1	1735.1	1761.4	1660.7	1711.1	1892.8	1897.1

[a]Indicates excitations added to problem configurations where applicable.
[b]Indicates problem configurations.
[c]Not applicable.

Unfortunately, for the $6p$ attachment a single configuration is not sufficient as we have convergence problems in the negative ion while using $4f5d6s^26p$ only. As a result the $5d\langle r\rangle$ is $\sim$0.5 a.u. larger in the negative ion than in the neutral. Fortunately, test calculations on core-valence effects show correlation from $5p$,$5d$ pairs in this case have an energy contribution of $\sim$320 meV, but only a few meV difference between the negative on states and the neutral threshold.

Our basis set includes configurations involving all single and double excitations out of the outer valence space $5d/6s/6p$ electrons. The $4f$ electron is treated as part of the core and has single occupancy throughout the calculation. The $4f$ $\langle r\rangle$ is found to be consistent (1.05 to 1.15 a.u.) throughout the neutral threshold and both parities of the negative ion, and test runs indicate only minor (few meV) differences in energy contribution for correlation configurations involving the $4f$ subshell.

Orbitals that are unoccupied in the MCDF configurations are represented by relativistic screened hydrogenic functions, whose effective Z, Z^*, are determined by energy minimization during the RCI procedure. The virtual orbitals are added in ''layers'' to configurations with large contributions until the basis is saturated (when a given virtual only adds a few

TABLE II. Energy contributions to Ce^- odd state ($5d$ attachment) electron affinities ($-$meV).

	Ce I $4f5d^26s$	Ce^- $4f5d^26s^2$						
Excitation	$^5I^o_8$	$^4H^o_{7/2}$	$^4H^o_{9/2}$	$^4I^o_{9/2}$	$^4H^o_{11/2}$	$^2G^o_{7/2}$	$^2G^o_{9/2}$	$^4I^o_{11/2}$
$6s\rightarrow s^a$	0.0	35.6	35.4	33.3	38.7	30.5	36.2	34.9
$6s\rightarrow d^a$	8.6	43.1	44.1	50.7	45.5	54.5	52.5	46.8
$6s\rightarrow g^a$	12.3	30.2	30.5	30.3	31.1	29.4	30.4	30.6
$5d\rightarrow s+d+g$	33.2	29.5	30.6	49.0	32.1	37.1	26.9	42.4
$6s^2\rightarrow s^2$	NA[c]	29.5	29.5	29.5	29.6	29.0	29.0	29.7
$6s^2\rightarrow p^{2\ b}$	NA[c]	430.6	429.7	430.1	428.0	429.0	428.4	429.5
$6s^2\rightarrow d^2+f^2+g^2$	NA[c]	22.4	22.6	22.8	23.3	22.3	22.8	22.8
$5d6s\rightarrow p^{2\ a,b}$	6.3	236.6	236.9	243.4	240.3	229.5	230.9	240.8
$5d6s\rightarrow sd^{a,b}$	55.0	119.9	120.8	122.4	123.1	120.9	121.8	122.3
$5d6s\rightarrow pf^{a,b}$	162.4	246.9	247.6	249.2	250.7	246.7	247.3	250.1
$5d6s\rightarrow d^2+f^2+g^2+dg$	6.9	19.2	19.2	18.8	19.7	18.8	19.0	19.2
$5d^2\rightarrow d^{2\ a}$	41.3	45.7	45.8	44.2	44.4	50.3	49.3	43.9
$5d^2\rightarrow f^{2\ a}$	33.3	35.2	35.4	33.0	32.8	42.4	40.5	31.9
$5d^2\rightarrow s^2+p^2+g^2+sd+dg+pf$	26.1	22.4	22.1	22.7	21.8	28.3	24.4	21.4
Total	385.4	1346.7	1350.1	1379.3	1360.2	1368.6	1359.4	1366.2

[a]Indicates excitations added to problem configurations where applicable.
[b]Indicates problem configurations.
[c]Not applicable.

TABLE III. Electron affinities (meV) and LS composition for Ce^- bound states. The first number in parentheses is the percent of the leading term. LS terms with less than one percent are omitted. Δ_{2O} indicates shift in Ce^- energies (in meV) when second order effects are removed.

Level (LS %)	EA (this work)	Δ_{2O}	EA (prior work [3])
$^2H^e_{9/2}$ (62,^{4}I 19,^{2}G 15,^{4}H 3,^{4}G 1)	349	90	259
$^2G^e_{7/2}$ (80,^{4}H 14,^{2}F 3,^{4}F 2,^{4}G 1)	215	80	147
$^4G^e_{5/2}$ (53,^{2}F 42,^{2}D 4,^{4}F 1)	203	91	105
$^4H^e_{7/2}$ (38,^{2}G 33,^{2}F 20,^{4}G 8,^{4}D 1)	153	85	55
$^2D^e_{3/2}$ (55,^{4}F 32,^{4}D 7,^{2}P 6)	135	74	43
$^2H^e_{11/2}$ (68,^{4}I 26,^{4}G 3,^{4}H 2,^{2}I 1)	117	97	
$^4I^e_{9/2}$ (57,^{2}G 37,^{4}F 3,^{4}H 1,^{4}G 1,^{2}H 1)	104	91	
$^2F^e_{7/2}$ (36,^{4}H 29,^{4}G 19,^{2}G 11,^{4}D 3,^{4}F 2)	53	81	
$^4H^o_{7/2}$ (75,^{2}G 24,^{2}F 1)	428	91	178
$^4H^o_{9/2}$ (68,^{2}G 28,^{2}H 3,^{4}F 1)	327	93	
$^4I^o_{9/2}$ (93,^{2}H 6,^{4}H 1)	281	95	
$^4H^o_{11/2}$ (56,^{4}I 39,^{2}I 4,^{2}H 1)	193	95	
$^2G^o_{7/2}$ (59,^{4}H 24,^{2}F 14,^{4}G 2,^{4}D 1)	182	92	
$^2G^o_{9/2}$ (68,^{4}H 28,^{4}F 2,^{4}G 2)	167	91	
$^4I^o_{11/2}$ (54,^{4}H 40,^{2}H 5,^{2}I 1)	149	95	

meV or less to the total configurational contribution). In the case of Ce^-, the first two sets of virtuals are complete, and a third set is added to select configurations. As the calculations progress we approach our 7000 basis member maximum, and small (in both coefficient and energy contribution) parents are removed. A typical final run has 6000–7000 parents and has had approximately 3000 small parents removed at various steps in the calculation.

III. RESULTS

Energy contributions from correlation configurations are given in Tables I and II for the $6p$ and $5d$ attachments, respectively. Also noted in Tables I and II are the problem configurations and the second order effects that were added for each parity. Note that much of the second order effects comes also from relaxing the J restriction on double excitations from the $6s^2$ subgroup (allowing $J>0$). It is worth noting that the problem configurations in Ce^- are the same type (same excitation) for both parities as in La^- [5].

The labeling of levels in Tables I and II is derived from the leading LS % which are calculated by creating approximate LS eigenstates at the DF level. The full LS breakdown is provided in Table III along with the EA's. Also shown for comparison in Table III are the EA's predicted in the earlier work [3], as well as the contribution by second order effects to the EA's in this work. In the $6p$ attachment case, $>90\%$ of the second order contribution is accounted for in retrieved contribution from the problem configurations. For the $5d$ case, $\sim 15\%$ of the second order effects comes from improvement of $6s$ single excitations due to the aforementioned $6s^2$ J restriction relaxation, and the bulk of the rest is from the problem cases as expected. Note that in the case of the $6p$ attachments, when the second order effects are removed there is good agreement between this work and the previous

TABLE IV. Ce^- allowed transition f values (length gauge).

Transition	f value (l)	Transition	f value (l)	Transition	f value (l)
$^4H^o_{7/2}\rightarrow{}^2H^e_{9/2}$	1.91×10^{-3}	$^4H^o_{9/2}\rightarrow{}^2G^e_{7/2}$	2.06×10^{-3}	$^2G^e_{5/2}\rightarrow{}^2G^o_{7/2}$	6.72×10^{-5}
$\rightarrow{}^2G^e_{7/2}$	6.04×10^{-3}	$\rightarrow{}^4H^e_{7/2}$	1.98×10^{-2}	$^4H^o_{11/2}\rightarrow{}^2H^e_{11/2}$	5.04×10^{-4}
$\rightarrow{}^4G^e_{5/2}$	3.30×10^{-2}	$\rightarrow{}^2H^e_{11/2}$	4.03×10^{-3}	$\rightarrow{}^4I^e_{9/2}$	1.31×10^{-3}
$\rightarrow{}^4H^e_{7/2}$	7.47×10^{-3}	$\rightarrow{}^4I^e_{9/2}$	2.54×10^{-2}	$^2G^o_{7/2}\rightarrow{}^4H^e_{7/2}$	1.92×10^{-3}
$\rightarrow{}^4I^e_{9/2}$	1.44×10^{-2}	$\rightarrow{}^2F^e_{7/2}$	3.19×10^{-2}	$\rightarrow{}^4I^e_{9/2}$	3.28×10^{-3}
$\rightarrow{}^2F^e_{7/2}$	7.58×10^{-3}	$^4I^o_{9/2}\rightarrow{}^2G^e_{7/2}$	4.83×10^{-3}	$\rightarrow{}^2F^e_{7/2}$	1.11×10^{-2}
$^2H^e_{9/2}\rightarrow{}^4H^o_{9/2}$	3.98×10^{-4}	$\rightarrow{}^4H^e_{7/2}$	1.19×10^{-7}	$^2G^o_{9/2}\rightarrow{}^4H^e_{7/2}$	2.37×10^{-5}
$\rightarrow{}^4I^o_{9/2}$	1.58×10^{-3}	$\rightarrow{}^2H^e_{11/2}$	1.19×10^{-7}	$\rightarrow{}^2H^e_{11/2}$	1.49×10^{-4}
$\rightarrow{}^4H^o_{11/2}$	4.39×10^{-5}	$\rightarrow{}^4I^e_{9/2}$	3.49×10^{-3}	$\rightarrow{}^4I^e_{9/2}$	5.89×10^{-3}
$\rightarrow{}^2G^o_{7/2}$	7.26×10^{-4}	$\rightarrow{}^2F^e_{7/2}$	1.92×10^{-2}	$\rightarrow{}^2F^e_{7/2}$	1.66×10^{-3}
$\rightarrow{}^2G^o_{9/2}$	4.34×10^{-3}	$^2G^e_{7/2}\rightarrow{}^2G^o_{7/2}$	1.30×10^{-3}	$^4I^o_{11/2}\rightarrow{}^2H^e_{11/2}$	3.38×10^{-4}
$\rightarrow{}^4I^o_{11/2}$	3.09×10^{-3}	$\rightarrow{}^2G^o_{9/2}$	3.06×10^{-4}	$\rightarrow{}^4I^e_{9/2}$	1.10×10^{-3}

paper [3] for the 5 levels that were originally reported (average difference of 10 meV), which is an indication that the second order effects have been the primary improvement in the calculations.

Finally, in Table IV we present electric dipole *f* values for the LS allowed transitions in Ce^-. The small energy differences involved here make accurate velocity gauge calculations difficult to obtain.

ACKNOWLEDGMENT

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

[1] S.H. Vosko, J.B. Lagowski, I.L. Mayer, and J.A. Chevary, Phys. Rev. A **43**, 6389 (1991).
[2] C. Froese Fischer, J. Lagowski, and S. Vosko, Phys. Rev. Lett. **59**, 2263 (1987).
[3] K. Dinov, D.R. Beck, and D. Datta, Phys. Rev. A **50**, 1144 (1994).
[4] A.M. Covington, D. Calabresse, J.S. Thompson, and T.J. Kvale, J. Phys. B **31**, L855 (1998).
[5] S.M. O'Malley and D.R. Beck, Phys. Rev. A **60**, 2558 (1999).
[6] S.M. O'Malley and D.R. Beck, Phys. Rev. A **57**, 1743 (1998).
[7] W.C. Martin, B. Zalubas, and L. Hagan, *Atomic Energy Levels, The Rare Earth Elements*, NSRDS-NBS60 (US GPO, Washington, DC, 1978).
[8] J.P. Desclaux, Comput. Phys. Commun. **9**, 31 (1975).