

# Autodetachment lifetime calculations of long lived metastable states of $\text{Ba}^-$ and $\text{Eu}^-$

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**Abstract.** A calculation of the autodetachment energy width of the decay of the  $\text{Ba}^-$   $5d6s6p\ ^4F_{9/2}$  metastable state to the  $6s^2\epsilon h_{9/2}$  continuum predicts a lifetime for this state of 0.18 s. The  $\text{Ba}^-$  calculation is used as a template for the more computationally intensive calculation of the analogous  $4f^75d6s6p\ J = 8$  metastable state of  $\text{Eu}^-$ . This state is predicted to lie  $11\,797\text{ cm}^{-1}$  above the  $4f^76s^2$   $\text{Eu I}$  ground state with a lifetime of 0.23 s. Opening of the 5p subshell in both cases and careful treatment of cancellation in the energy width calculations have been essential in obtaining these lifetimes.

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## 1. Introduction

In recent years Davis and Thompson have reported a series of measurements of electron affinities of rare earths in the range  $\sim 0.8$  to  $\sim 1.0$  eV, e.g.  $\text{Tm}^-$  [1],  $\text{Ce}^-$  [2], and  $\text{Eu}^-$  [3]. In some cases these values are  $\sim 0.5$  to  $\sim 0.9$  eV higher than earlier calculated electron affinities [4, 5]. While it is unlikely that a single explanation may be found to resolve the differences between experiment and theory in all these cases, our efforts have been directed toward studies of long lived excited states, most recently in  $\text{Tm}^-$  [6]. The supposition is that the experiments [1, 2, 3] may be measuring the difference between a metastable state of the negative ion and an excited threshold of the neutral atom rather than the true electron affinity (EA).

Improvements to our suite of continuum codes [7, 8] required to perform the  $\text{Tm}^-$  calculations [6] have led to further motivation to study autodetachment lifetimes for other metastable states. The case of the  $5d6s6p\ ^4F_{9/2}^o$  state of  $\text{Ba}^-$  is computationally interesting due to the fact that, at the Dirac-Fock (DF) level, it decays by autodetachment to the  $6s^2\epsilon h$  ground state continuum only by means of the Breit operator. The large  $l$  of the continuum function, determined by the total  $J$  of the state ( $J < 9/2$  would allow  $\epsilon f$  or  $\epsilon p$ ), combined with the fact that the autodetachment energy width is dominated by correlation in the negative ion and the neutral portion of the continuum state (for which the Coulomb operator gives a nonzero contribution), suggested a long lived (greater than  $1\ \mu\text{s}$ ) metastable state.

Storage ring experiments [9] eliminated the possibility of a lifetime in the range of  $\sim 100$ - $\sim 400\ \mu\text{s}$  for this  $\text{Ba}^-$  metastable state and thus suggested a lifetime range of

$\sim 5\text{--}\sim 100\ \mu\text{s}$  (the lower limit determined by lack of “a reduction of beam content of the  ${}^4F_{9/2}$  component during its passage of the equipment” [9]). Further analysis suggested that the  $5d6s6p\ {}^4F_{9/2}$  lifetime might lie *above* the  $\sim 100\text{--}\sim 400\ \mu\text{s}$  range, perhaps as large as 1-5 ms [10, 11]. Preliminary calculations by our group [12] essentially agreed with this 1-5 ms range, though much ambiguity remained due to the large amount of cancellation (three orders of magnitude or more) in the contributions to the autodetachment energy width and the limited correlation in the relativistic configuration interaction (RCI) wavefunctions used to calculate the width.

In this work we have expanded correlation in the  $Ba^-$  calculation in both the negative ion and neutral ground state, including opening the 5p subshell, and we have more carefully treated the cancellation in contributions to the energy width. Additionally, we have performed a much more complicated calculation of the autodetachment lifetime of the  $4f^7 5d6s6p\ J = 8$  metastable state of  $Eu^-$ , which decays to the  $4f^7 6s^2 \epsilon h$  ground state continuum. We find that the  $4f^7$  subgroup in this calculation is sufficiently core-like and isolated from the rest of the valence electrons, that the two systems are essentially analogous in terms of which correlation configurations are important to the energy width calculations.

For this  $Eu^-$  metastable state to be seen by Davis and Thompson, it must live at least  $\sim 50\ \mu\text{s}$  [1, 2, 3], and while they report an EA for the  $Eu^-$  ground state of 1.053 eV [3], an earlier experiment (based on relative yields) by Nadeau *et al.* estimated  $Eu^-$  to be bound to the  $Eu\ I$  ground state by  $>0.050\ \text{eV}$  [13]. Preliminary RCI calculations of this EA were hampered by lack of convergence of the multi-configurational Dirac-Fock (MCDF) calculation [14] which produces our DF one electron radial functions. Difficulty in generation of these DF radial functions is typical of systems that are unbound or weakly bound (by a few tens of meV), so this result tends to agree with the smaller EA value.

## 2. Methodology

### 2.1. RCI and energy width calculations

The negative ion wavefunction is produced by a typical RCI calculation of the  $5d6s6p\ J = 9/2\ Ba^-$  state, while the composition of the continuum state wavefunction is derived from an RCI calculation of the  $Ba\ I\ 6s^2$  ground state. The coefficients of the various correlation configurations in the continuum state (e.g.  $6p^2 \epsilon h$ ,  $5d^2 \epsilon h$ , ...) are determined by the corresponding coefficients in this  $Ba\ I$  calculation ( $6p^2$ ,  $5d^2$ , ...). Though our current methodology does not allow mixing of different continuum functions, these calculations are not affected as the  $5d6s6p\ J = 9/2$  state (at  $8434\ \text{cm}^{-1}$ [9]) lies below the lowest excited  $Ba\ I$  state ( $5d6s\ {}^3D_1$  at  $9034\ \text{cm}^{-1}$ [15]), so only the ground state channel is open, and another continuum function with higher  $l$  (e.g.  $\epsilon k$ ) cannot make  $J = 9/2$ .

Our one electron radial wavefunctions are produced by a multi-configuration Dirac-

Fock (MCDF) calculation using Desclaux's code [14]. The many electron basis functions of our RCI calculations are linear combinations of determinants ( $\Delta_i$ , antisymmetrized many body wavefunctions) of these one electron wavefunctions,

$$\phi = \sum_i \alpha_i \Delta_i, \quad (1)$$

where the coefficients,  $\alpha_i$ , are determined by requiring that the RCI basis functions be eigenfunctions of  $J^2$ ,  $J_z$ , and parity. The final correlated RCI wavefunctions are, of course, linear combinations of these basis functions,

$$\psi = \sum_j \beta_j \phi_j, \quad (2)$$

where the coefficients,  $\beta_j$ , are determined by diagonalization of the Hamiltonian matrix.

To include correlation in this final wavefunction with configurations that contain subshells not present in the DF configuration of the negative ion or neutral calculation, we use virtual one electron radial functions, which we denote  $vl$ . These functions are relativistic screened hydrogenic functions with a single variable parameter,  $Z^*$ , the effective nuclear charge. Within the RCI calculations, these virtual functions are necessarily orthogonalized to each DF radial function (as well as previously added virtual functions) of the same symmetry, and the  $Z^*$  for each virtual is determined by energy minimization.

The autodetachment lifetime calculation is a relativistic extension [16] of the methodology of Fano [17]:

$$\tau \text{ (s)} = \frac{2.4189 \times 10^{-17}}{2\pi |\langle \Psi | H_{DB} - E | U(E) \rangle|^2}, \quad (3)$$

where  $\Psi$  is the localized negative ion RCI wavefunction, and  $U(E)$  is the nonlocalized wavefunction constructed by combining the neutral RCI wavefunction with an  $\epsilon h_{9/2}$  continuum function generated by the continuum wavefunction solver (CONTWVSA) of Perger *et al.* [7, 8]. In the  $Ba^-$  case the energy of the continuum function ( $8434 \text{ cm}^{-1}$ ) is taken from experiment [9]. For  $Eu^-$  we made a separate set of RCI calculations treating the  $Eu^- 4f^7 5d 6s 6p J = 8$  state as a  $6p_{3/2}$  attachment to the  $Eu I 4f^7 5d 6s {}^{10}D_{13/2}$  excited state [18]. The binding energy of the  $Eu^-$  metastable state with respect to this threshold places it at  $11797 \text{ cm}^{-1}$  above the  $Eu I 4f^7 6s^2 {}^8S_{7/2}$  ground state (and thus below the lowest excited state at  $12924 \text{ cm}^{-1}$  [18]).

The Hamiltonian,  $H_{DB}$ , in (3) is the full Dirac-Breit Hamiltonian, and the resonance energy  $E$  is effectively removed from the calculation by excluding possible diagonal cases in the matrix elements. For example, in  $Ba^-$  the neutral portion of  $U(E)$  is restricted to  $J = 0$ , so correlation configurations in the ket that contain a  $vh$  subshell are carefully constructed to omit the equivalent basis functions, e.g.  $[5d^2]_{J=0}vh$  (which appears in the bra as  $[5d^2]_{J=0}\epsilon h$ ). While the entire denominator in (3) constitutes the autodetachment energy width,  $\Gamma$ , for purpose of analysis it is simpler to track contributions to the  $H_{DB}$  matrix elements themselves. Thus, where contributions to these  $H_{DB}$  matrix elements are found to have cancellations of three orders of magnitude, this is essentially a cancellation of six orders of magnitude in  $\Gamma$  (or  $\tau$ ).

The matrix elements of  $H_{DB}$  are set up by a modified version of our main RCI code [19]. The matrix element for each pair of interacting basis functions in the bra and ket is tabulated in terms of relativistic Coulomb radial integrals,

$$R^k(a, b|c, d) = \int_0^\infty \int_0^\infty [P_a^*(1)P_c(1) + Q_a^*(1)Q_c(1)] \frac{r_1^k}{r_{12}^{k+1}} [P_b^*(2)P_d(2) + Q_b^*(2)Q_d(2)] dr_1 dr_2, \quad (4)$$

and similar integrals involving the Breit operator. To complete the data preparation to evaluate the matrix elements of  $H_{DB}$ , the coefficient of each radial integral in each bra-ket basis pair must be multiplied by the corresponding coefficient of the basis function from each of the separate negative ion and neutral RCI calculations as well as by the overlap integrals for any non-orthonormal (NON) subshells excluded from the radial integral (an in depth discussion of our partial treatment of NON in the use of our suite of continuum codes is provided elsewhere [6]; see section 2.2 for further discussion of NON issues specifically applicable to these calculations). Finally, coefficients for each radial integral are summed over all the bra-ket basis pairs (so that each integral is only evaluated once), and the integrations are performed by the continuum integral solver (CIS) code of Perger *et al.* [20].

## 2.2. One electron radial basis sets

A fully automated autodetachment/autoionization code with full treatment of NON is gradually being created by our group out of the several continuum function codes and data preparers mentioned above. Currently, our codes allow a partial treatment of NON that assumes that corresponding orbitals in the bra and ket are reasonably orthonormal (overlap 0.85-1.00), in which case noncorresponding orbitals are treated as orthogonal. For example, the overlap integral  $\langle 6s|6s \rangle$  ( $\sim 0.95$ ) is taken into account when two slightly different radial basis sets are used for the bra and ket. However, the overlap  $\langle vs|6s \rangle$  is treated as zero in our current setup, whereas a full NON treatment allows expansion of the bra and ket radial functions in terms of a transformed common set of radial functions [21]. Errors introduced by using only partial NON are small provided two conditions are met: the overlap integrals of noncorresponding orbitals are small (say  $\sim 0.20$  or less), and cancellation in the  $H_{DB}$  matrix elements is reasonably minor (perhaps one order of magnitude at most). If these two criteria are met, the relative error introduced is approximately equal to the square of the overlap of the noncorresponding orbitals. The problem is further mitigated in cases where the weight of individual correlation configurations in the bra or ket are small ( $\sim 0.1\%$  or less), since the error relative to the DF contribution is also multiplied by the small coefficients of the correlation configuration.  $Ba^-$  and  $Eu^-$  are special cases in regard to these criteria in that the DF configurations in the bra and ket interact only through the Breit operator, so the calculation of the energy width is dominated by interaction of correlation configurations. Additionally, the largest  $H_{DB}$  matrix elements are found to have as much as three orders of magnitude cancellation among radial integrals.

Intermediate stages in the  $Ba^-$  calculations exhibited drastic changes in some

correlation configuration matrix elements, e.g. as much as a doubling or halving of the contribution with the introduction of a second set of virtual orbitals or a difference of only a few configurations between subsequent calculations. Since the largest changes seemed to occur wherever two sets of calculations had differing sets of  $Z^*$  parameters in their virtual basis sets, a series of calculations designed to estimate the “missing pieces” due to partial treatment of NON was performed. For example, the matrix elements of the form  $\langle 6s6pvg | H_{DB} | 6s^2\epsilon h \rangle$  are calculated in the partial NON method and include the overlap between the differing 6s radial functions,  $\langle 6s | 6s \rangle$ . A corresponding test calculation replacing the  $\langle 6s | 6s \rangle$  overlap with the  $\langle vs | 6s \rangle$  overlap ( $\sim 0.15$ ) and using the  $vs6pvg$  coefficients from the  $Ba^-$  calculation, then showed that a piece of the calculation that was being omitted in the partial NON treatment was actually of similar size ( $\sim 40\%$  of the piece that was expected to dominate the calculation).

Since the lifetime calculation is extremely sensitive to differences in the the two radial basis sets, we have instead used a common basis set for the negative ion and neutral RCI calculations. This choice is possible primarily due to the fact that the neutral DF radial functions dominate the wavefunction in valence stage calculation, e.g.  $6svs$  and  $vs^2$  in the Ba I valence calculation have correlation energies  $\ll 1$  meV and weights of the order of  $10^{-6}$ . We have built our radial basis sets up by using the core through 5d, 6s, and 6p radial functions from the neutral MCDF calculation [14]. A second set of valence DF radial functions are included by adding  $5d'$ ,  $6s'$ , and  $6p'$ , which are taken from the negative ion MCDF calculation [14] and are necessarily orthogonalized to all other radial functions of the same symmetry already present, e.g.  $5d'$  actually has the general form of a 6d wavefunction after orthogonalization to 3d, 4d, and 5d.

Inclusion of the primed set of DF radial functions is required to provide corrections to the unprimed set of valence DF radial functions in the negative ion calculation. Since we no longer have 5d, 6s, and 6p radial functions optimized to the  $5d6s6p$  state, corrections in the form of single electron replacements ( $5d'6s6p$ ,  $5d6s'6p$ , and  $5d6s6p'$ ) account for approximately 1.35 eV of correlation required to bring our final negative ion calculations within  $\sim 10$  meV of the total energy of a corresponding calculation using radial functions optimized to  $5d6s6p$  (which justifies our use of the alternative radial basis with regard to energy minimization concerns). In general, it would be possible to use a set of diffuse (small  $Z^*$ ) virtual radial functions in place of these primed DF radial functions, but doing so results not only in diffuse  $vs$ ,  $vp$ , and  $vd$  radial functions but also diffuse  $vf$  and  $vg$  functions as part of the single electron replacements  $6p \rightarrow vf$  and  $5d \rightarrow vg$  in the correlation configurations  $5d6svf$  and  $6s6pvg$ . The autodetachment lifetimes are highly sensitive to these two configurations because they are effectively double replacements to the  $6s^2\epsilon h$  ground state configuration of the form  $sh \leftrightarrow df + pg$ , which are large correlation effects due to the similarity of  $\Delta l$  between the pairs of electrons. By including the primed set of DF radial functions, which are optimized to  $5d6s6p$ , our RCI energy minimization process results in  $Z^*$ 's for  $vf$  and  $vg$  similar to those in the negative ion calculation with the “correct” DF radial functions, and we avoid

the possibility of artificially inflating the impact of  $5d6s\nu f$  and  $6s6p\nu g$  in the lifetime calculation (more diffuse  $\nu f$  and  $\nu g$  interact more with the nonlocalized  $\epsilon h$  continuum function).

Our first set of virtual radial functions is then chosen to optimize the negative ion RCI calculation. Those same  $Z^*$ 's are used in the neutral calculation without readjustment to minimize its energy, which has little impact ( $\ll 1$  meV) in the valence calculation, as mentioned above. The second and final set of virtual orbitals are added with the opening of the 5p subshell, and are allowed to differ (by optimization through energy minimization) between the negative ion and neutral calculations. Since all the radial functions up to this point are common between the two calculations, only these final corresponding radial function overlaps ( $\langle \nu s' | \nu s' \rangle$ ,  $\langle \nu p' | \nu p' \rangle$ , etc.) differ from 1.00, and there are no longer any “missing pieces” since our treatment of NON is now complete by design, e.g.  $\langle \nu s | 6s \rangle = 0$ .

### 2.3. Creation of RCI basis functions

At first glance, the  $Eu^-$  calculation appears insurmountable given the capabilities of our current RCI code [19]: a maximum of 20 000 basis functions with a total number of determinants limited to 1 M. The properties of the system work to our advantage, however. First, there is negligible mixing between configurations with different angular momenta in the outer valence electrons, specifically there is no component of  $4f^7 5d6s$  in the  $4f^7 6s^2$  ground state. This allows us to restrict the outer valence electrons to  $J = 0$  in the neutral calculation and  $J = 9/2$  in the negative ion calculation. Second, test calculations show that basis functions for the  $4f^7$  subgroup are nearly pure  $^8S$  [18], allowing us to restrict this subgroup to  $J = 7/2$ .

While the RCI method is fully relativistic, we have the capability of introducing approximate LS basis functions via a linear transformation of our original  $j$ - $j$  coupled basis functions. The procedure requires a diagonalization of the  $L^2 + S^2$  matrix with the assumptions that the minor components of the one electron wavefunctions are small and that the major components are largely independent of  $j$ . An LS analysis of the  $Eu^-$  and  $Eu$  I DF configurations shows mixing of the  $^6P_{7/2}$  term in the  $4f^7$  subgroup is  $\sim 1\%$ , and mixing of all other terms is negligible (several orders of magnitude less). So while the  $4f^7$  subgroup contains 50  $j$ - $j$  basis functions, with a proper transformation, we can retain just 2 LS basis functions, and our  $Eu^-/Eu$  I calculations are only twice as large as rather than 50 times larger than the  $Ba^-/Ba$  I calculations in terms of total RCI basis size. The savings is not as great in terms of determinants, however, as 64 of the 237  $j$ - $j$  determinants are required to create the two  $^8S$  and  $^6P$  basis functions of the  $4f^7$  subgroup.

Our current usage of LS basis functions in our RCI code [19] is limited to fairly simple DF configurations, with a maximum of 100 basis functions containing 1000 determinants or fewer. Since the number of basis functions and determinants of the remaining portion of each configuration are multiplied by the 50 basis functions and 237

determinants of the  $4f^7$  subgroup to get the totals for the complete  $Eu^-/Eu$  I relativistic configuration, the current code would allow for the second subgroup to consist of only 2 basis functions with a maximum of 4 determinants between them. A more extensive method of RCI data preparation, which allows splitting of more complicated relativistic configurations into two parts [22], does not have the capability of producing LS basis functions, and it is not easily modified to do so as it produces data one relativistic configuration at a time, while creation of LS functions requires transformation of all the  $j$ - $j$  functions of the corresponding nonrelativistic configuration at once. For these  $Eu^-$  and  $Eu$  I calculations to remain manageable in scope, we must create LS basis functions for every configuration, not just a few of the simplest ones. For this reason a separate data preparer, a modified version of the RCI code [19], was created to expand the LS function creation to 500 basis functions with 5000 determinants. Once the LS functions are created using the full set of  $j$ - $j$  basis members, the 1/25 of the functions that are kept (using 64/237 of the determinants) are read into the larger RCI calculation.

Approximately 300 LS files are required to set up both of the final RCI calculations, and many of the larger configurations have processing times of two hours or more on a 500 MHz Alpha workstation. Fortunately, a simplification in the data preparation can be realized by considering the coupling of two angular momenta [23],

$$|JM\rangle = (-1)^{j_1-j_2-M} \sqrt{2J+1} \sum_{m_1, m_2} \begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix} |j_1 m_1, j_2 m_2\rangle. \quad (5)$$

In the case that  $J = j_1 + j_2$  and  $M = +J$ , there is only one term in the above sum, and the entire Clebsch-Gordon coefficient reduces to 1. Other  $M$ 's with the same  $J$  can be created from this case using the step-down operator. Since we meet the above criteria in  $Eu^-$  ( $J = 8 = 7/2 + 9/2$ ) and  $Eu$  I ( $J = 7/2 = 7/2 + 0$ ), the combination of the two subgroups becomes trivial. A single file can be created for the  $4f^7$  subgroup using the external LS data preparation code (retaining only  $^8S$  and  $^6P$ ) and the second subgroup of each configuration can be created separately much and more economically ( $\sim 30$  seconds per file). Once the data for the subgroups is created, preparation of all 300 combined input files by a simple auxiliary code takes less than 10 minutes. This process is also useful in preparing the nonlocalized  $U(E)$  wavefunction from (3) by combining the  $Ba$  I or  $Eu$  I basis functions with a simple file containing the single (one determinant)  $h_{9/2}$  basis function.

#### 2.4. Correlation configurations

Valence correlation configurations include all single and double excitations out of the negative ion  $5d6s6p$  subgroup and the neutral  $6s^2$  subgroup. Virtual subshells in the neutral calculations are included up to  $l = 4$  ( $vg$ ). In the negative ion calculations the last virtual set is extended to include  $vh$  and  $vi$  radial functions, allowing potentially large correlation effects in the matrix elements of  $H_{DB}$  such as  $dh+\pi i \leftrightarrow sh$ .

The decision to open the core is primarily due to the poor positioning of the nearest excited states in the neutral calculations. For example, in  $Ba$  I the first excited even

$J = 0$  state is  $5d^2$  at  $23\,209\text{ cm}^{-1}$  above the  $6s^2$  ground state [15]. A calculation including only valence correlation results in a first excited state  $1011\text{ cm}^{-1}$  higher than experiment with nearly equal mixing of  $5d^2$  and  $6p^2$ . Inclusion of core-valence correlation in the form of  $5p5d$ ,  $5p6s$ , and  $5p6p$  pair excitations yields a first excited state that is 92% pure  $5d^2$  with an error in energy position of  $210\text{ cm}^{-1}$ . Of course, our goal is to ensure the proper mixing of  $5d^2$  and  $6p^2$  in the ground state wavefunction, since these are the two most important ket correlation functions in the energy width calculation. In the Ba I case the effect is a shift of  $5d^2/6p^2$  mixing in the ground state of 0.4%/3.6% in the valence calculation to 1.0%/2.1% in the more correlated final calculation.

In the negative ion calculations, full treatment of the opening of the  $5p$  subshell is difficult for two reasons. First, the number of basis functions quickly exceeds our 20 000 limit, given inclusion of all potentially large core-valence and  $5p$  single and double excitations. Second, there are several valence configurations important to the energy width (e.g.  $6p^2vf$ ,  $5d^26p$ ,  $6s6pvg$ , and  $5d6svf$ ) which must be given equal treatment with  $5s6s6p$  to avoid disturbing their relative positions and weights in the  $Ba^-$  final wavefunction. Due to these difficulties, we have decided to use the criterion that any correlation involving  $5p$  should have a first order interaction with the DF configurations or important valence correlation configurations in both the bra and ket, ensuring that these configurations will have both a reasonably large weight and a potentially large  $H_{DB}$  matrix element. This criterion excludes double excitations from the  $5p$  subshell in both cases, and imposes the restriction that such correlation in the bra contains a subgroup of  $5d^2$ ,  $6s^2$ , or  $6p^2$  with  $J = 0$ , greatly reducing the size of the negative ion RCI basis set. This correlation from the core in the bra is small ( $\sim 20\text{ meV}$ ), so the relative composition of the important valence configurations is undisturbed. In the ket calculation, this selection criterion results in exactly the type of core-valence correlation discussed above, ensuring the correct mixture of  $5d^2$  and  $6p^2$  in the final ket wavefunction.

### 3. Results

#### 3.1. Autodetachment energy width contributions

Contributions to the energy width are presented in table 1 in the form of collections of  $H_{DB}$  matrix elements. The entries represent summations over all configurations of the same symmetry, so “spd” in the bra includes the DF configuration,  $5d6s6p$ , as well as single and double replacements such as  $5d'6s6p$  and  $5dvs6p$  (it is simpler to group contributions in the RCI calculations as these configurations use the same LS files discussed in section 2.3). Of course, the  $f^7$  subgroup is implied in the  $Eu^-$  bra and ket. We note that, in general, there is a correspondence between the two systems as to which bra-ket configuration combinations have large matrix elements, reinforcing the idea that  $4f$  subshell is isolated enough from the remaining  $Eu^-$  valence electrons to treat the systems as analogous. The “Valence” columns represent calculations as

complete as the “Final” ones (in terms of size of the radial basis set), but with the 5p subshell closed. The difference in the two sets of columns is primarily due to differing weights of  $5d^2$ ,  $6p^2$ , and  $6s6s'/6svs$  in the bra.

The size of our final  $Eu^-$  RCI basis set is 4282 functions, far less than the coded limit of 20 k but equivalent to  $\sim 107$  k  $j-j$  functions given our reduction in basis size by use of the LS input. Because of the restrictions placed on our core excitations discussed in section 2.4, the  $Eu$  I calculation actually has the largest number of determinants,  $\sim 933$  k, which is the equivalent of  $\sim 3.5$  times our code maximum of 1 M had we used the full  $j-j$  basis set.

From the table 1, we can note that inclusion of the  $v_h$  and  $v_i$  radial function in the ket reduced the lifetimes by  $\sim 20\%$ . While inclusion of the Breit operator in  $H_{DB}$  has affected the  $Ba^-$  lifetime by about the same amount ( $\sim 98\%$  of the contribution from Breit integrals is in the bra DF contributions), the DF contribution in  $Eu^-$  has essentially cancelled. No immediate reason for this difference is evident, though given the amount of cancellation involved, differences of this size between the two systems can easily be attributed to differences in the continuum functions (their energies differ by  $\sim 33\%$ ). Inclusion of the Breit operator in the  $Ba^-$  RCI calculations were found to alter the mixing of important configurations only minimally, as the effect on the lifetime was  $\sim 1\%$ . Estimates derived from small test calculations suggest that the larger contributions to the energy width might be affected by  $\sim 5\%$  by retaining the  ${}^6P$  LS term in the  $Eu^-/Eu$  I calculations. Given the relative mixing of the LS terms that were omitted, errors introduced by doing so are likely two orders of magnitude smaller than the last digit presented in the energy contributions of table 1.

While the contributions to the energy width from core excitations are large,  $\sim 30\%$  of the largest valence contributions, approximately 85% of this energy is from interactions with the  $(4f^7)5p^55d6s6p_h$  configuration in the ket. The weight of the  $(4f^7)5p^55d6s6p$  configuration in the neutral RCI calculations is  $\sim 0.9\%$  in  $Ba$  I and  $\sim 0.6\%$  in  $Eu$  I, nearly as large as the important  $5d^2$  and  $6p^2$  valence configurations, so these large contributions are not unexpected. In order to ensure our criterion for selection of core correlation presented in section 2.4 is reasonable, we performed a series of limited test calculations expanding the  $Ba^-$  basis. The largest additional contributions not present in our final calculations came from inclusion of core-valence double excitations in the ket that were not restricted to inclusion of a  $5d^2$ ,  $6s^2$ , or  $6p^2$   $J = 0$  subgroup, and these contributions totaled  $\sim 0.05 \times 10^{-9}$  a.u.,  $\sim 1\%$  of the total energy width contribution. These same test calculations resulted in negligible ( $\sim 0.01\%$ ) changes in the composition of the negative ion wavefunction, suggesting that the mixing of important configurations is in much better shape at the valence stage than in the neutral calculation.

### 3.2. Cancellation

Table 2 displays an example of cancellation in the  $H_{DB}$  matrix elements from one of the larger contributions from table 1. Note the tendency for  $R^k$  integrals containing

the two relativistic radial functions from a nonrelativistic subshell to cancel each other. Normally, when we speak of saturation in an RCI calculation it is in terms of saturating the energy contribution of a given correlation configuration by including another set of virtual radial functions in the configuration. At intermediate stages of these autodetachment lifetime calculations we have noticed a saturation of cancellation in the corresponding  $R^k$  integrals in contributions to the energy width. That is, differences in  $R^k$  integrals containing  $5d_{3/2}$  and  $5d_{5/2}$  radial functions were somewhat mitigated by adding  $vd$  or  $vd'$  radial functions. This led to a more careful treatment of the primed DF radial functions that were taken from the negative ion MCDF calculations.

Originally, since the negative ion  $J = 9/2$   $5d6s6p$  DF configuration contains only  $5d_{5/2}$  and  $6p_{3/2}$ ,  $5d^26p$  was included in the MCDF calculation in order to generate  $5d_{3/2}$  and  $6p_{1/2}$  functions. The resulting  $5d$  and  $6p$  functions were sufficiently different to cause problems with these cancellation effects. For example, the  $\langle r \rangle$  of the  $6p_{3/2}$  and  $6p_{1/2}$  radial functions in  $Ba^-$  were  $\sim 7.9$  and  $\sim 6.3$  a.u., respectively. Rather than using such disparate radial functions, we have taken the extra primed radial functions from a separate  $5d6s6p$   $J = 7/2$  calculation ( $4f^75d6s6p$   $J = 7$  for  $Eu^-$ ) in which the  $6p_{1/2}$  ( $\langle r \rangle \sim 7.8$ ) and  $5d_{3/2}$  are better optimized to the  $5d6s6p$  configuration rather than  $5d^26p$ . This change of primed radial functions combined with the common radial basis discussed in section 2.2 are the essential improvements in the cancellation within the energy widths that produce final lifetime results in the tenths of seconds, rather than  $\sim 10$  ms.

### 3.3. Conclusion

The predicted lifetimes of 0.18 s and 0.23 s for the metastable states of  $Ba^-$  and  $Eu^-$  are extremely sensitive to cancellations in the matrix elements of the autodetachment energy width. More thorough treatment of NON and core-valence correlation results in the cancellation in the energy width calculations that produces these lifetimes greater than a tenth of a second. Preliminary calculations excluding these improvements showed variations of a factor of 2 at subsequent stages of the basis set construction and produced much shorter lifetimes in the range of 1-10 ms. Our final methodology is more stable in the later stages of our lifetime calculations, varying less than 10% between subsequent calculations and giving greater confidence in the longer lifetimes presented here.

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**Table 1.** Largest valence configuration contributions (magnitude greater than  $10^{-10}$  a.u.) to autodetachment energy widths. “Final” calculations include correlation from opening the 5p subshell, and “Valence” calculations are shown to illustrate the impact of this opening of the shallow core. Energies are presented in units of  $10^{-9}$  a.u.

Contributions	Final		Valence	
	Ba <sup>-</sup>	Eu <sup>-</sup>	Ba <sup>-</sup>	Eu <sup>-</sup>
$\langle \text{spd}   H_{\text{DB}}   \text{s}^2 \epsilon \text{h} \rangle$	-0.57	-0.13	-0.60	-0.13
$\langle \text{spd}   H_{\text{DB}}   \text{p}^2 \epsilon \text{h} \rangle$	0.07	0.22	0.10	0.28
$\langle \text{spd}   H_{\text{DB}}   \text{d}^2 \epsilon \text{h} \rangle$	-0.09	-0.12	-0.06	-0.09
$\langle \text{p}^2 \text{f}   H_{\text{DB}}   \text{p}^2 \epsilon \text{h} \rangle$	0.57	2.96	0.61	2.78
$\langle \text{pd}^2   H_{\text{DB}}   \text{p}^2 \epsilon \text{h} \rangle$	-0.33	-1.70	0.14	-1.01
$\langle \text{pd}^2   H_{\text{DB}}   \text{d}^2 \epsilon \text{h} \rangle$	0.19	0.07	0.41	-0.10
$\langle \text{spg}   H_{\text{DB}}   \text{s}^2 \epsilon \text{h} \rangle^{\text{a}}$	5.68	6.62	0.16	0.60
$\langle \text{spg}   H_{\text{DB}}   \text{p}^2 \epsilon \text{h} \rangle$	0.64	1.16	0.23	0.37
$\langle \text{pdg}   H_{\text{DB}}   \text{p}^2 \epsilon \text{h} \rangle$	0.18	-0.42	-0.12	-0.41
$\langle \text{pdg}   H_{\text{DB}}   \text{d}^2 \epsilon \text{h} \rangle$	0.33	0.21	0.03	0.03
$\langle \text{sdf}   H_{\text{DB}}   \text{s}^2 \epsilon \text{h} \rangle$	-2.84	-5.99	1.61	-0.32
$\langle \text{sdf}   H_{\text{DB}}   \text{d}^2 \epsilon \text{h} \rangle$	0.11	0.20	0.07	0.15
$\langle \text{d}^2 \text{f}   H_{\text{DB}}   \text{d}^2 \epsilon \text{h} \rangle$	-0.08	0.14	0.08	0.21
$\langle \text{pf}^2   H_{\text{DB}}   \text{p}^2 \epsilon \text{h} \rangle$	-0.17	0.00	0.08	0.22
$\langle \text{spi}   H_{\text{DB}}   \text{s}^2 \epsilon \text{h} \rangle$	-0.32	-0.57	0.01	0.07
$\langle \text{sdh}   H_{\text{DB}}   \text{s}^2 \epsilon \text{h} \rangle$	-0.20	-0.29	0.02	0.05
Other Valence	-0.16	-0.24	0.00	-0.04
Core	1.65	2.00		
Total	4.46	4.12	2.77	2.66
Lifetime (s)	0.18	0.23	0.50	0.54

<sup>a</sup>This contribution is used as an example of cancellation in table 2.

**Table 2.** Example of cancellation in  $Ba^-$  autodetachment energy width: largest contributions (magnitude greater than  $10^{-8}$  a.u.) to  $\langle \text{spg} | H_{DB} | s^2 \epsilon h \rangle$ . Energies are presented in units of  $10^{-9}$  a.u. with cancellation illustrated by adding corresponding  $R^k$  integrals containing  $g_{9/2}$  and  $g_{7/2}$  and then further combining corresponding integrals containing  $p_{3/2}$  and  $p_{1/2}$ . The total for the  $R^k$  integrals shown is 5.78 a.u., compared to 5.68 a.u. for the full  $\langle \text{spg} | H_{DB} | s^2 \epsilon h \rangle$  contribution (see table 1).

Contributions to $\langle \text{spg}   H_{DB}   s^2 \epsilon h \rangle$		$\Sigma g$	$\Sigma p$
$R^1(vg_{9/2}, 6p_{3/2}   \epsilon h_{9/2}, 6s_{1/2})$	2766.68		
$R^1(vg_{7/2}, 6p_{3/2}   \epsilon h_{9/2}, 6s_{1/2})$	-2754.34	12.34	
$R^1(vg_{9/2}, 6p_{1/2}   \epsilon h_{9/2}, 6s_{1/2})$	-2818.40		-0.69
$R^1(vg_{7/2}, 6p_{1/2}   \epsilon h_{9/2}, 6s_{1/2})$	2805.37	-13.03	
$R^1(vg_{9/2}, 6p'_{3/2}   \epsilon h_{9/2}, 6s_{1/2})$	795.18		
$R^1(vg_{7/2}, 6p'_{3/2}   \epsilon h_{9/2}, 6s_{1/2})$	-790.06	5.12	
$R^1(vg_{9/2}, 6p'_{1/2}   \epsilon h_{9/2}, 6s_{1/2})$	-830.68		-0.44
$R^1(vg_{7/2}, 6p'_{1/2}   \epsilon h_{9/2}, 6s_{1/2})$	825.12	-5.56	
$R^1(vg'_{9/2}, 6p_{3/2}   \epsilon h_{9/2}, 6s_{1/2})$	-90.18		
$R^1(vg'_{7/2}, 6p_{3/2}   \epsilon h_{9/2}, 6s_{1/2})$	88.45	-1.73	
$R^1(vg'_{9/2}, 6p_{1/2}   \epsilon h_{9/2}, 6s_{1/2})$	88.95		-0.09
$R^1(vg'_{7/2}, 6p_{1/2}   \epsilon h_{9/2}, 6s_{1/2})$	-87.31	1.64	
$R^1(vg'_{9/2}, 6p'_{3/2}   \epsilon h_{9/2}, 6s_{1/2})$	113.84		
$R^1(vg'_{7/2}, 6p'_{3/2}   \epsilon h_{9/2}, 6s_{1/2})$	-114.73	-0.89	
$R^1(vg'_{9/2}, 6p'_{1/2}   \epsilon h_{9/2}, 6s_{1/2})$	-114.92		-0.05
$R^1(vg'_{7/2}, 6p'_{1/2}   \epsilon h_{9/2}, 6s_{1/2})$	115.76	0.84	
$R^4(6p_{3/2}, vg_{9/2}   \epsilon h_{9/2}, 6s_{1/2})$	-160.93		
$R^4(6p_{3/2}, vg_{7/2}   \epsilon h_{9/2}, 6s_{1/2})$	161.40	0.47	
$R^4(6p_{1/2}, vg_{9/2}   \epsilon h_{9/2}, 6s_{1/2})$	167.21		5.76
$R^4(6p_{1/2}, vg_{7/2}   \epsilon h_{9/2}, 6s_{1/2})$	-161.92	5.29	
$R^4(6p'_{3/2}, vg_{9/2}   \epsilon h_{9/2}, 6s_{1/2})$	-147.42		
$R^4(6p'_{3/2}, vg_{7/2}   \epsilon h_{9/2}, 6s_{1/2})$	145.28	-2.14	
$R^4(6p'_{1/2}, vg_{9/2}   \epsilon h_{9/2}, 6s_{1/2})$	145.96		1.54
$R^4(6p'_{1/2}, vg_{7/2}   \epsilon h_{9/2}, 6s_{1/2})$	-142.28	3.68	
$R^1(vg_{9/2}, 6p_{3/2}   \epsilon h_{9/2}, 6s'_{1/2})$	-162.72		
$R^1(vg_{7/2}, 6p_{3/2}   \epsilon h_{9/2}, 6s'_{1/2})$	162.03	-0.69	
$R^1(vg_{9/2}, 6p_{1/2}   \epsilon h_{9/2}, 6s'_{1/2})$	165.50		0.03
$R^1(vg_{7/2}, 6p_{1/2}   \epsilon h_{9/2}, 6s'_{1/2})$	-164.78	0.72	
$R^1(vg_{9/2}, 6p'_{3/2}   \epsilon h_{9/2}, 6s'_{1/2})$	-47.61		
$R^1(vg_{7/2}, 6p'_{3/2}   \epsilon h_{9/2}, 6s'_{1/2})$	47.33	-0.28	
$R^1(vg_{9/2}, 6p'_{1/2}   \epsilon h_{9/2}, 6s'_{1/2})$	49.29		0.02
$R^1(vg_{7/2}, 6p'_{1/2}   \epsilon h_{9/2}, 6s'_{1/2})$	-48.99	0.30	
$R^4(6p_{3/2}, vg_{9/2}   \epsilon h_{9/2}, 6s'_{1/2})$	10.80		
$R^4(6p_{3/2}, vg_{7/2}   \epsilon h_{9/2}, 6s'_{1/2})$	-10.81	-0.01	
$R^4(6p_{1/2}, vg_{9/2}   \epsilon h_{9/2}, 6s'_{1/2})$	-11.14		-0.30
$R^4(6p_{1/2}, vg_{7/2}   \epsilon h_{9/2}, 6s'_{1/2})$	10.85	-0.29	