Computational Methods in Lanthanide and Actinide Chemistry
Computational Methods in Lanthanide and Actinide Chemistry

Edited by

MICHAEL DOLG

Institute for Theoretical Chemistry,
University of Cologne, Germany

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Contributors

Raymond Atta-Fynn, Department of Physics, University of Texas, Arlington, USA

Jochen Autschbach, Department of Chemistry, University at Buffalo, State University of New York, USA

Zoila Barandiarán, Department of Chemistry, Autonomous University of Madrid, Spain.

Enrique R. Batista, Theoretical Division, Los Alamos National Laboratory, USA

Donald R. Beck, Department of Physics, Michigan Technological University, USA

Eric J. Bylaska, Pacific Northwest National Laboratory, USA

Xiaoyan Cao, Theoretical Chemistry, University of Cologne, Germany

Ludovic Castro, Laboratory of Physics and Chemistry of Nano-Objects, National Institute of Applied Sciences, France

Carine Clavaguéra, Laboratoire de chimie moléculaire, Département de chimie, École Polytechnique CNRS, France

Wibe A. de Jong, Lawrence Berkeley National Laboratory, USA

Jean-Pierre Dognon, Laboratoire de Chimie Moléculaire et de Catalyse pour l’énergie, CEA/Saclay, France

Michael Dolg, Institute for Theoretical Chemistry, University of Cologne, Germany

Kenneth G. Dyall, Dirac Solutions, USA

Ephraim Eliav, School of Chemistry, Tel Aviv University, Israel

Niranjan Govind, Pacific Northwest National Laboratory, USA

Uzi Kaldor, School of Chemistry, Tel Aviv University, Israel
Contributors

Christos E. Kefalidis, Laboratory of Physics and Chemistry of Nano-Objects, National Institute of Applied Sciences, France

Andrew Kerridge, Department of Chemistry, Lancaster University, UK

Laurent Maron, Laboratory of Physics and Chemistry of Nano-Objects, National Institute of Applied Sciences, Toulouse, France

Richard L. Martin, Theoretical Division, Los Alamos National Laboratory, USA

Hiroko Moriyama, Graduate School of Natural Sciences, Nagoya City University, Japan

Steven M. O’Malley, Atmospheric and Environmental Research, USA

Lin Pan, Physics Department, Cedarville University, USA

Lionel Perrin, Laboratory of Physics and Chemistry of Nano-Objects, National Institute of Applied Sciences, France

Kirk A. Peterson, Department of Chemistry, Washington State University, USA

Pekka Pyykkö, Department of Chemistry, University of Helsinki, Finland

Florent Réal, Université Lille CNRS, Laboratoire PhLAM, CNRS UMR 8523, France

Trond Saue, Laboratoire de Chimie et Physique Quantiques, Université Paul Sabatier (Toulouse III), France

Bernd Schimmelpfennig, Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology (KIT), Germany

Luis Seijo, Department of Chemistry, Autonomous University of Madrid, Spain.

André Severo Pereira Gomes, Université Lille CNRS, Laboratoire PhLAM, CNRS UMR 8523, France

Lidia Smentek, Department of Chemistry, Vanderbilt University, USA

Hiroshi Tatewaki, Graduate School of Natural Sciences, Nagoya City University, Japan

Valérie Vallet, Université Lille CNRS, Laboratoire PhLAM, CNRS UMR 8523, France

Lucas Visscher, Theoretical Chemistry, Amsterdam Center for Multiscale Modeling, VU University Amsterdam, The Netherlands
Contributors

Ulf Wahlgren, Department of Physics, Stockholm University, AlbaNova University Centre, Sweden

John W. Weare, Department of Chemistry and Biochemistry, University of California San Diego, USA

Anna Weigand, Theoretical Chemistry, University of Cologne, Germany

Florian Weigend, Karlsruhe Institute of Technology, Germany

Ahmed Yahia, Laboratory of Physics and Chemistry of Nano-Objects, National Institute of Applied Sciences, France

Shigeyoshi Yamamoto, School of International Liberal Studies, Chukyo University, Japan

Ping Yang, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory (PNNL), USA
Preface

Lanthanides and actinides comprise about one-quarter of the known chemical elements collected in the periodic table. Because of their complex electronic structure, the significant electron correlation effects, and the large relativistic contributions, the f-block elements are probably the most challenging group of elements for electronic structure theory. In 1987 Pyykkö reviewed the available relativistic electronic structure calculations for f-element molecules (Inorganica Chimica Acta 139, 243–245, 1987). Of the 59 listed studies, 53 dealt with actinides and only 10 with lanthanides. The applied computational methods comprised \textit{ab initio} Dirac-Hartree-Fock one-center expansion and Dirac-Hartree-Fock-Slater calculations, quasirelativistic all-electron \( \alpha \)-studies, and semiempirical valence-only approaches like relativistic extended Hückel theory. None of these studies took into account static electron correlation explicitly using a multi-configurational wavefunction or included at an \textit{ab initio} level the effects of dynamic electron correlation. No applications of modern density functional theory to f-element molecules were reported either. The treatment of relativity included the Dirac one-particle relativity in a few cases explicitly, but mostly in some approximate form, whereas corrections due to the Breit two-particle interaction or arising from quantum electrodynamics were entirely neglected. Relativistic effective core potentials were only available for a few actinides, which certainly also hampered a routine exploration of lanthanide and actinide chemistry with quantum chemical approaches.

Tremendous progress was made in dealing with lanthanide and actinide systems since the 1987 review of Pyykkö appeared, and the field continues to develop quickly. The current book aims to provide the reader an overview of those state-of-the-art electronic structure theory approaches that have been successfully used for f-element systems so far and summarizes examples of their application. The 16 chapters were written by leading experts involved in the development of these methods as well as their application to various aspects of f-element chemistry. From the results of several studies discussed in these contributions it becomes apparent that quantum chemists successfully conquered the field of lanthanide and actinide chemistry and can provide very valuable contributions not merely supplementing experimental studies, but also frequently guiding their setup and explaining their outcome. Moreover, with largely improved theoretical methods and computational resources at hand, it also became possible to obtain new insights with respect to the interpretation of the electronic structure of f-element compounds.

Despite these many encouraging developments, it is appropriate to say that when it comes to lanthanides and actinides modern electronic structure theory currently can accomplish many things, but certainly not all. It is also clear that this book can only provide a snapshot of the current state of affairs. A number of promising computational approaches, e.g., local electron correlation schemes or F12-dependent wavefunctions, are currently developed and already successfully applied to non-f-element systems. They will during the next years most
likely significantly extend the array of available methods for quantum chemical studies of lanthanides and actinides. Thus more exciting developments can be anticipated.

Finally I would like to thank all authors of the chapters for their excellent contributions. My thanks also go to the staff at Wiley, i.e., Sarah Higginbotham, Sarah Keegan, and Rebecca Ralf, for their guidance and support during this book project. Last but not least, I’m grateful to Mrs. Peggy Hazelwood for copy-editing and to Mr. Yassar Arafat at SPI for final handling of the proofs.

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1

Relativistic Configuration Interaction Calculations for Lanthanide and Actinide Anions

Donald R. Beck\textsuperscript{1,*}, Steven M. O’Malley\textsuperscript{2} and Lin Pan\textsuperscript{3}

\textsuperscript{1}Department of Physics, Michigan Technological University
\textsuperscript{2}Atmospheric and Environmental Research
\textsuperscript{3}Physics Department, Cedarville University

1.1 Introduction

Lanthanide and actinide atoms and ions are of considerable technological importance. In condensed matter, they may be centers of lasing activity, or act as high temperature superconductors. Because the $f$-electrons remain quite localized in going from the atomic to the condensed state, a lot of knowledge gained from atoms is transferable to the condensed state. As atoms, they are constituents of high intensity lamps, may provide good candidates for parity non-conservation studies, and provide possible anti-proton laser cooling using bound-to-bound transitions in anions such as La$^-$ [1].

In this chapter we will concentrate on our anion work [2–4], which has identified 114 bound states in the lanthanides and 41 bound states in the actinides, over half of which are new predictions. In two anions, Ce$^-$ and La$^-$, bound opposite parity states were found, making a total of 3 [Os$^-$ was previously known]. Bound-to-bound transitions have been observed in Ce$^-$ [5] and may have been observed in La$^-$ [6]. We have also worked on many properties of lanthanide and actinide atoms and positive ions. A complete list of publications can be found elsewhere [7].

*Corresponding author. E-mail: donald@mtu.edu

1.2 Bound Rare Earth Anion States

In 1994, we began our first calculations on the electron affinities of the rare earths [8]. These are the most difficult atoms to treat, due to the open $f$-subshells, followed by the transition metal atoms with their open $d$-subshells. At that time, some accelerator mass spectrometry (AMS) measurements of the lanthanides existed [9, 10] which were rough. Larger values might be due to multiple bound states, states were uncharacterized as to dominant configuration, etc.

Local density calculations done in the 1980s had suggested anions were formed by $4f$ attachments to the incomplete $4f$ subshell. Pioneering computational work done by Vosko [11] in the early 1990s on the seemingly simple Lu$^-$ and La$^-$ anions using a combination of Dirac-Fock and local density results suggested instead that the attachment process in forming the anions involved $p$, not $f$, electrons.

Our 1994 calculation on a possible Tm anion was consistent with this, in that it showed $4f$ attachment was not a viable attachment process. Our calculations are done using a Relativistic Configuration Interaction (RCI) methodology [12], which does a Dirac-Hartree-Fock (DHF) calculation [13] for the reference function ($s$) (dominant configurations). The important correlation configurations (e.g., single and pair valence excitations from the reference configuration[s]) are then added in, using the DHF radials and relativistic screened hydrogenic function (called virtuals), whose effective charge ($Z^*$) is found by minimization of the energy matrix, to which the Breit contributions may be added, if desired.

Experience gained in the mid-1990s suggested that good candidates for bound anion states might be found by combining observed ground and excited state neutral spectra with the computational knowledge that closing an $s$-subshell might lower the energy $\sim 1.0$ eV or adding a $6p$-electron to a neutral atom state ($7p$ in the actinides) might lower the energy $\sim 0.25$ eV. The variety of energetically low-lying configurations in the observed spectrum of Lu and Ce suggests a potential for a large number of bound anion states, which has now been computationally confirmed.

As an example of the process, a Tm$^-$ $4f^{14}6s^2$ anion state might be bound if there were a $4f^{14}6s^1$ state observed in the neutral atom that was less than 1 eV above the ground state. The use of excited states with $s/p$ attachment also has the computationally attractive feature that it avoids, to a good level of approximation, having to compute correlation effects for $d$ and/or $f$ electrons. An $s$ attachment to an excited state can be equivalent to a $d$ attachment to the ground state. The angular momentum expansions for such pair excitations converge slowly, and a lot of energy is associated with (nearly) closed $d$ and/or $f$ subshells. Clearly, it is best to reduce such problems if usable experimental results exist.

It has always been our position to use no more than moderately size $d$ wavefunction expansions. Current limits are about 20,000 symmetry adapted wavefunctions built from fewer than 1 million Slater determinants, and use of two virtuals per $l$, per shell ($n$). This allows the “physics” (systematics) to be more visible and reduces the need for “large” computational resources that were frequently unavailable in the “old” days. Development of systematic “rules” is one of the main goals of our research. Some examples follow: (i) determining which correlation effects are most important for a specific property [14, 15], (ii) near conservation of $f$-value sums for nearly degenerate states [15, 16], (iii) similar conservation of $g$-value sums [16], (iv) similar conservation of magnetic dipole hyperfine constants [17, 18]. This approach does mean near maximal use of symmetry, creating extra auxiliary
computer codes, and increases the necessity of automating data preparation and file manipulation. Much stricter development of this automation is one of the two factors that reduced calculation of the entire actinide row to less than the time it used to take to complete the calculation for one anion (>4 months for Nd\(^-\)). Use of moderately sized wavefunctions also requires careful selection of which property-specific configurations to include and careful optimization of the virtual radial functions.

1.3 Lanthanide and Actinide Anion Survey

In 2008 and 2009 our group presented a series of three papers [2–4] representing an unprecedented and complete survey of the bound lanthanide and actinide anion states predicted by valence level RCI calculations. The first of these [2] was a study of all 6\(p\) attachments to \(4f^n 6s^2\) ground and excited states of the lanthanide neutral spectra (then and throughout the discussion here we use \(n\) as an occupancy of \(N-2\) where \(N\) is the total number of valence electrons in the neutral atom configuration, including the core-like \(4f/5f\) subshells). The second paper [3] completed the lanthanide survey with 6\(p\) attachments to \(4f^m 5d 6s^2\) thresholds and 6\(s\) attachments to \(4f^m 5d^2 6s\) thresholds (\(m \equiv N-3\)). The final paper in the series [4] included the equivalent 7\(s\) and 7\(p\) attachments to corresponding actinide neutral thresholds as well as additional states in Th\(^-\) and Pa\(^-\) representing 7\(p\) attachments to \(5f^q 6d^2 7s^2\) thresholds (\(q \equiv N-4\)). The approach used to handle the complexity of these calculations represented the culmination of over three decades of group experience in developing techniques and computational tools for RCI basis set construction. The path that led to this comprehensive lanthanide and actinide anion survey was somewhat circuitous and developed originally through adjustments to increasing difficulties with each step toward more complex systems. In the following subsections we discuss some milestones leading up to the survey, the computational issues and solutions, the improved analytical tools that were needed, and a summary of results of the survey.

1.3.1 Prior Results and Motivation for the Survey

Throughout the 1990s and early 2000s our group had been steadily pushing our methodology towards more and more complex atomic systems. The ability to do so was partly from techniques described in Section 1.3.2 but also largely due to ever-increasing computer power. Mid-row transition metal studies had become fairly routine, e.g., binding energies of Ru\(^-\) [19], Os\(^-\) [20], and Tc\(^-\) [21]. However, the added complexity of a near-half-full\(f\) subshell over that of a \(d\) had relegated us for the most part to the outer edges of the lanthanide and actinide rows, e.g., Ce\(^-\) [22, 23], Th\(^-\) [24], Pr\(^-\) [25], U\(^-\) [26], Pa\(^-\) [27], La\(^-\) [28], and Lu\(^-\) [29]. During the mid- to late-1990s, we were twice enticed by the unique case of Tb to attempt to skip to the center of the lanthanide row [30]. The Tb ground state is \(4f^9 6s^2\), but the low-lying first excited state (~35 meV [31]) is of the opposite parity \(4f^8 5d 6s^2\) configuration, and the possibility of opposite parity Tb\(^-\) bound anion states resulting from the same 6\(p\) attachment mechanism was a tempting prize. Unfortunately, those initial attempts at this mid-row anion were premature and Tb\(^-\) would have to wait to use basis set construction techniques that we eventually developed in the mid-2000s.
As we were gradually working our way inwards from the ends of the lanthanide and actinide rows, our papers began to take on a back-and-forth dialog with the work of the experimental atomic physics group at University of Nevada, Reno (Thompson and co-workers) usually within our accessible range of elements, e.g., La$^-$ [32], Lu$^-$ [33], Tm$^-$ [34], Ce$^-$ [35], Pr$^-$ [36], but occasionally outside our purview in the mid-row, e.g., Eu$^-$ [37] (although this case is a much more approachable problem than it may appear at first glance since the 4f$^7$ electron subgroup can be effectively restricted to 8S and 9P terms [3]). This observation coupled with a similar result in our work on Eu$^-$ auto-detachment lifetimes in metastable states [38] helped lead to the realization that angular momentum couplings of the 4f$^n$ subshell could be considerably restricted with little accuracy loss, with great gains in computational efficiency (see Section 1.3.2.2). The Reno group employed the laser photodetachment electron spectroscopy (LPES) technique, which relies upon identification of peaks in the kinetic energy spectrum of detached photoelectrons, and their electron affinities were often considerably higher than contemporary AMS values [39]. Of particular interest to us were the many features in their published Ce$^-$ spectrum [35], and a brief overview of the history of the electron affinity measurements and computations for Ce$^-$ will perhaps set the stage to better illustrate the wide gap in predicted/measured values between our two groups and the importance of their eventual reconciliation.

In the early 1990s, AMS experiments such as Garwan et al. [9] had detected Ce$^-$, and high yields seemed to indicate a large electron affinity (>0.6 eV) or several moderately bound states. At the time, density functional theory computations of Vosko et al. [11] were suggesting that Ce$^-$’s (and other lanthanides’) bound states would be formed by 6p and possibly 5d attachments rather than 4f as previously assumed. Our earliest Ce$^-$ calculations in 1994 studied both of these attachments to the 4f 5d 6s$^2$ ground state configuration and predicted a 4f 5d 6s$^2$ 6p Ce$^-$ anion ground state with electron affinity of 259 meV. These calculations also predicted four additional bound even states and an odd 4f 5d$^2$ 6s$^2$ state with a binding energy of 178 meV. In 1997 Berkovitz et al. used a combination of laser excitation and AMS techniques to obtain a measured electron affinity of 700(10) meV. In the midst of our renewed push towards the center of the lanthanide and actinide rows, we revisited our RCI Ce$^-$ computations in 2000 [23]. A recent re-dimensioning of our main RCI code [12] allowed us to now include extensive second-order effects. These took the form of relaxed $j$ restrictions on electron subgroups and configurations representing triple/quadruple replacements with respect to the configurations of interest; no direct impact on their energies, only indirect through lowering of nearby single/double replacement (first-order) configurations. These results flipped the predicted RCI ground state to 4f 5d$^2$ 6s$^2$ with an electron affinity increased to 428 meV with an additional six odd bound excited states and eight even 4f 5d 6s$^2$ 6p bound states with largest binding energy of 349 meV. Just when the gap between experiment and theory seemed to be improving, Davis and Thompson (Reno group) reported their 2002 measurements [35] with an LPES electron affinity of 955(26) meV and at least two excited states at 921(25) and 819(27) meV. By 2004, Cao and Dolg [40] had produced their own computational results using the relativistic energy-consistent small core pseudo-potential methodology that predicted the same 4f 5d$^2$ 6s$^2$ ground state configuration with an electron affinity of 530 meV.

In 2006, we again revisited Ce$^-$ with the RCI methodology [41]. This time we were able to include some limited core-valence correlation involving the 5s and 5p subshells and the careful use of a high J excited neutral threshold to define the relative positions of
the anion manifolds with respect to the neutral ground state configuration. (We will see in Section 1.3.3 that the latter introduced its own difficulties.) The result was an increase in the RCI electron affinity to 511 meV in good agreement with the recent Cao and Dolg value, but this latest RCI study also resulted in an astounding 26 bound anion states for both parities. Despite these advancements, there seemed to be no missing elements in our bases that could possibly account for the near doubling of the two computational results to approach the experimental values of Davis and Thompson.

Discussions with Thompson [42] suggested that the remaining difference of \( \sim 450 \) meV might be a misinterpretation of the most prominent feature of their photoelectron kinetic energy spectrum when they used it as the anion ground state to neutral ground state transition. In fact, some crude initial photodetachment calculations suggested that one should expect the most prominent feature to be from the \( 4f^5 5d^2 6s^2 \) ground state configuration detaching via \( 6s \) to \( \varepsilon_p \) leaving the neutral atom in a \( 4f^5 5d^2 6s \) excited state. Based on this idea, the experimental analysis would be off by \( \sim 350 \) meV, but the two sets of computations were also still too low by \( > 100 \) meV. We performed an ambitious set of cross section computations for all our bound anion states to all neutral thresholds within the range of the 2.410 eV experimental incident photon energy [35] using a frozen core approximation. By using the experimental photon energy, we were able to simulate an expected spectrum by adding together Gaussian peaks at each transition energy scaled by the appropriate relative cross sections and a few different effective anion temperature distributions. The Gaussian width was arbitrarily adjusted until the scaled simulated spectrum produced a best qualitative fit to the experimental data (i.e., subjective “by eye” comparison), and alignment of the prominent peaks then produced an effective electron affinity of 660 meV. The re-analysis was met with enthusiasm from the experimenters [43], and additional experimental results from Walter et al. [44] using tunable laser photodetachment threshold spectroscopy with incident photon energies in the range of 610-750 meV produced an electron affinity of \( \sim 650 \) meV. We thus regarded this Ce\(^-\) case as an excellent example of theory and experiment working together toward a common goal of understanding a particularly complex atomic anion. Section 1.4 discusses more recent work on Ce\(^-\) photodetachment cross section.

Having made the case for the usefulness of simulated spectra in analysis of photodetachment studies, we endeavored to take the next step in other systems, the intention being to provide additional computational details beyond simple binding energy numbers. Our Nd\(^-\) work from early 2008 [45] was this next step. It was successful in the sense that much like Ce\(^-\), detachment to higher excited state configurations was found to be much more likely, provided an experimenter attempted an LPES study with the same 2.410 eV incident photon energy that had been used by Davis and Thompson [35]. In this case \( 4f^6 6s^2 6p \) anion states were found to detach with much higher cross section via \( 6s \) to \( \varepsilon_p \) leaving the neutral atom in excited \( 4f^6 6s \ 6p \) states rather than a \( 6p \) detachment back to the neutral \( 4f^6 6s^2 \) ground state configuration (primarily due to resonances arising from coincidence with the incident energy and the excited threshold positions). Of course, more practically the real effect of this result was to warn an experimenter to instead choose a lower photon energy to avoid these \( 4f^6 6s \ 6p \) thresholds altogether.

In the long run, the most important products of this Nd\(^-\) study were the tools that were developed to help deal with basis set construction and jls restrictions placed on the \( 4f^4 \) electron subgroup. We had reached that limit where necessity had forced us to invent a new approach in order to move further into the row. Having gone through the pains of developing
a new technique to piece together multi-electron basis members (see Section 1.3.2), it wasn’t until we began to select the next project that we realized just how powerful was the approach that had been applied to Nd\(^{−}\). The analysis of \(4f^n\) subgroup composition could be left to fairly straightforward, manageable computations (few configurations) on each neutral atom, and the compositional analysis and basis selection for the remaining portion of the anion and neutral states could be performed on a system near the end of a row and systematically reapplied to all the elements of the row, including near the center where a full un-trimmed basis set would be orders of magnitude larger than our 20k limit. These techniques lent themselves particularly well to binding energy studies where analysis need only be done on basis set composition and energy contribution, as opposed to including additional criterion based on contributions to hyperfine structure, transition probabilities, or photodetachment cross sections. Because the cross section computations had by far taken up the bulk of CPU and human time in the Ce\(^{−}\) and Nd\(^{−}\) projects, it was not too difficult a decision to temporarily forgo that avenue of inquiry in favor of returning to pure binding energy studies, particularly now that doing so meant the opportunity to study whole rows of heavy elements in the 6-8 months we had typically spent on one anion.

### 1.3.2 Techniques for Basis Set Construction and Analysis

The robustness of the RCI methodology lies primarily in the flexibility of basis set construction. The process begins with the generation of 1-electron basis functions by solving the multi-configurational Dirac-Fock (MCDF) equations using Desclaux’s program [13]. In order to do Dirac-Fock calculations on a reference manifold for rare earths (and transition metals), the number of \(R^k\) integrals allowed was increased to 500K, the integrals were stored on disk, and the number of configuration state vectors (called “parents”) was increased to 1000. The structure input is produced by our RCI code [12]. To extrapolate from fractional \(Z(> N+1)\) down to \(N+1\), so necessary for anions, \(Z\) was converted from an integer to a real variable. At each stage in the basis set construction we are free to select or omit individual functions as needed while considering the delicate balance of reduction in basis size vs shift in energy positions (typically we aim for losses of less than a few meV if possible). The following sections describe the basis set construction and analytical tools in more detail.

#### 1.3.2.1 Simple Omission of “Small” Basis Members

At any particular stage in the development of an RCI basis set, one is typically adding correlation in one of several potential forms. It is important to saturate the 1-electron virtual basis typically up to two or three virtuals of each symmetry, so one could be adding, say \(v\pi\) when \(v\sigma\) and \(v\pi'\) are already present. One could also be extending the virtuals to higher \(l\), e.g., correlation of the form \(5d\ 6p\) to \(v\pi\) \(v\sigma\) has been found to be significant, so the equivalent \(5d\ 6p\) to \(v\pi\) \(v\sigma\) is tried. Often one includes second order effects after determining the importance of first order correlation, e.g., \(6s^2\) to \(v\pi\) \(v\pi'\) replacements from a \(5d^1\ 6s^2\) configuration is typically a large contributor to correlation, and adding the triple replacement \(5d\ 6s^2\) to \(v\pi\) \(v\sigma\) \(v\pi'\) will have no direct impact on the zeroth order configuration but may lower the double replacement and increase its contribution. Finally, if the system is not too complex (open valence electrons or close to full subshells), one may have room to add some core-valence effects, e.g., \(5p\ 6s\) to \(v\pi\) \(v\sigma\) in a transition metal \(5d^1\ 6s^2\) calculation.
Regardless of the “trial” that is being performed, one would typically perform an analysis of energy contributions using intermediate normalization \[46\] and RCI coefficients of individual basis members and make decisions on how much to trim the new basis set before moving on to the next step. For a particular J calculation this requires careful removal of basis members with little contribution in all levels of interest. When considering more than a few levels, the effectiveness of simple removal of basis functions can lose much of its usefulness as the set of functions small in all levels of interest is much smaller than the set of small contributors for any particular level. If one is concerned about using the wavefunction to compute some other property, impact on that calculation needs to be considered as well, e.g., transition probabilities to several potential initial or final states of other J-parity calculations. Although useful, even on a simple system, this approach can only trim an RCI basis size by a factor of $\sim 2–3$ at most. For the lanthanide and actinide survey we are discussing here, we needed an order of magnitude or more for the mid-row anions to make the calculations feasible.

1.3.2.2 Applying $jls$ Restrictions to $4fn,m$ Subgroups

One of the insights into our early Tb$^-$ calculations had been the realization that the $4f^9 6s^2 6p^2$ calculation had negligible mixing of any basis functions that did not restrict the $4f^9$ group of electrons to $j = 15/2$. With hindsight this is now obvious given that it was an attachment to the $4f^9 6s^2 J = 15/2$ neutral ground state. In our work on Nd$^-$ we did LS analysis of the anion vs. neutral $4f^4$ composition. Although the RCI method is purely relativistic, we can approximate LS states or LS terms on subgroups by straightforward rotation of the $jj$ basis set based on an approximate diagonalization of $L^2 + S^2$ applied to the spinors’ major components. The rotation does not affect the completeness of the basis. For Nd$^-$ we developed an auxiliary code that allowed us to make such a rotation of the $jj$ basis of the MCDF portion of an RCI calculation’s wavefunction after the fact in order to obtain both $jj$ and $ls$ analyses. It was then that we began to realize the strong connection between $4f^4$ composition between anion and neutral states.

At the time our RCI program \[12\] had two optional approaches to generate basis functions within the program. The first was a full-configuration option that was typically applied to a single relativistic configuration (e.g., $4f^{10}$) but could also include all relativistic configurations that made up a non-relativistic one (e.g., $4f^4 6s^2 6p^2$) to allow this pseudo-rotation to an LS basis on the full configuration or $ls$ terms within a subgroup. To use the latter option one necessarily complicates the basis set because all basis functions now contain mixing of all the determinants instead of just the ones from individual relativistic configurations (which is why one would want to do the LS analysis after the fact as mentioned above).

The second approach split a non-relativistic configuration into two parts, created determinant information on the two groups, and then pasted them together. This necessarily requires a range of $js$ for each piece, and a pasting together based on total $J$ of the calculation and combinations using standard angular momentum vector coupling theory. For Nd$^-$ the natural split is to separate $4f^4$ from the remaining 3-electron group of each correlation configuration.

The first option happened to be more limited in terms of the complexity of the size of the configuration it could handle. The second could handle a ten fold larger set of basis
functions, but it didn’t support the LS rotation option. Since our analysis was suggesting that an overall set of jls restrictions on 4f^4 would give us the edge we needed to allow a reasonable amount of valence correlation within our 20k limit, we extracted the method with the LS-rotation option to an external program where it could be re-dimensioned without adversely affecting other aspects of the RCI program. This auxiliary code [47] allows output to be read seamlessly. Even with this improvement, some of the more complicated correlation functions were running into memory limits and taking a day or more to complete.

As we began to think about next steps towards more complex anions, we realized that this new approach needed further improvement. It made no sense to keep re-creating the same 4f^{n,m} ls terms for each configuration. The process could also benefit from automation since files were being generated by hand and were vulnerable to typos. Ultimately, we ended up creating a database of partial configuration files. Using the program just described, we generated 4f^{n,m} and remaining 3- and 4-electron groups for this survey separately as if they were full configurations.

A second auxiliary code was then developed that would take a list of files for each part and, given the range of js for each piece and desired total J, piece together complete configurations with jls restrictions on the 4f^{n,m} part and relativistic jj bases on the remaining part. Further scripting and analysis was developed to scan an RCI program input file, recognize which external files would need to be available, and auto-generate a script to piece them together. This hybrid approach was an order of magnitude faster in CPU time and the human time and saved likely several months of tedious file editing.

1.3.2.3 Improvements of 1-Electron Bases in p Attachments

The MCDF calculation of our 1-electron bases includes an energy minimization of a specified level within each J-parity combination [13]. In order to generate a solution for anion states, one typically needs to step the nuclear charge down from some fractional value slightly greater than the actual Z of the anion, reusing the solutions from each previous step as an initial estimate. In the case of a p_1/2 attachment the singly occupied p_1/2 subshell of the final iteration in the process (the one with the correct integer Z), will be quite diffuse, but not overly so compared to the other d and s valence subshells (∼1 a.u. beyond the s). However, the p_3/2 subshell generated by this optimized calculation will typically have drifted to a much more diffuse ⟨r⟩ with a difference of >1 a.u. compared to ∼0.1 a.u. typical of pairs of relativistic subshells in neutral or multiply-occupied anion subshells. The opposite is true for an optimization to a p_3/2 attachment.

This disparity of the ⟨r⟩ of the outer DF p subshells became problematic when we began to add correlation involving p virtuals. If the MCDF radials were optimized to a p_1/2 level, we would see large correlation contributions from the single replacement p to vp_3/2 configuration in a p_3/2 attachment, indicating that energy minimization of our vp orbitals was selecting Z^∗ to act as a correction to the poorly optimized DF p_3/2 radial. The disparity in DF ⟨r⟩ propagated through the virtual ps as the j = 1/2 radials would have much higher Z^∗ than the corresponding j = 3/2 radial.

Our solution to this issue was to allow mixed 1-electron radial bases with outer DF p radials each taken from a computation optimized to a corresponding attachment, avoiding either of the diffuse orbitals that had “drifted away.” This works because as the RCI program reads in the 1-electron radial functions it performs an additional Gram-Schmidt orthogonalization
outwardly through all functions of each symmetry. Using these mixed radial bases allows
the virtual ps to then properly optimize important double replacement configurations rep-
resenting \( s p \) to \( vs \ vp + vp vd \). The result was useful for basis set construction because we
were then able to stop at two sets of virtuals, i.e., \( vp \) and \( vp' \).

1.3.2.4 Notation Conventions for Analysis

In dealing with the large number of bound states reported in this survey [2–4] it was use-
ful to develop some shorthand notations when describing composition of anion levels. In
addition to the typical total LS breakdown within the dominant MCDF configurations (with
total J indicated on the leading term only for simplicity), we included composition within
an alternate \( jj \) basis selected to reveal the mixing of attachment mechanism within each
state. For \( p \) attachments we denoted a \( p_{1/2} \) attachment term as \( "(j)" \), where \( j \) is the value for
the neutral \( f^m s^2 \) or \( f^m d^2 \) portion of the anion wavefunction. The \( p_{3/2} \) attachments were
distinguished by use of braces instead of parentheses: \( \"\{j\}\" \). By rounding the contributions
to integer percent we were able to convey a great deal of information on level composition
within fairly concise tables. For example, the Pr\(^-\) ground state was simply described by two
sets of compositions [2]: \( 5K5 \ 77, \ 3I \ 21, \ 5I \ 3, \ 3H \ 1 \) and \( \"(9/2) \ 99, \ [9/2] \ 1.\" \)
When it came to \( s \) attachments to excited \( f^m d^2 \) \( s^2 \) excited neutral thresholds, it was not
possible to split the \( s^2 \) subgroup in the anion to separate out the neutral portion of the
wavefunction. Instead, we approached the \( s \)-attachment analysis by providing similar \( jj \)
composition within our neutral wavefunctions, minus the \( s \) electron, i.e., on the \( f^m d^2 \) sub-
group. To distinguish from the \( p \) attachments we here used angled brackets in our notation:
\( \langle j \rangle \). For example, in Gd\(^-\) the two lowest \( 4f^7 \ 5d^2 \ 6s \) levels, \( ^{11}F_2 \) and \( ^{11}F_3 \), were described
by their \( 4f^7 \ 5d^2 \) composition as \( \langle 3/2 \rangle \ 88, \ \langle 5/2 \rangle \ 12 \) and \( \langle 5/2 \rangle \ 86, \ \langle 7/2 \rangle \ 14 \)\), respectively.
By investigating this composition, we thus showed that the two lowest \( 4f^7 \ 5d^2 \ 6s^2 \) levels,
\( ^{10}F_{3/2} \) and \( ^{10}F_{5/2} \), can be characterized primarily as \( 6s \) attachments to the \( J = 2 \) and \( J = 3 \)
thresholds, respectively.

1.3.3 Discussion of Results

In developing our basis sets for this survey, the leap to tackling entire rows of the periodic
table at once was predicated by the profound realization that the composition of bound anion
states’ \( f^{m,m} \) electron subgroups remained consistent with those of the corresponding low-
lying neutral thresholds to which we were attaching. In transition metals we used to treat \( d \)
attachments to \( d^2 s^2 \) neutral ground states as \( s \) attachments to excited \( d^{2+1} s \) levels to avoid
need to include the large disruption of perhaps multiple \( eV \) of correlation energy in \( d^2 \)
pair replacements. (These should have small anion-to-neutral differences when comparing
levels with the same \( d \) occupancy of \( x + 1 \) in this example.) This is an actual description of
the anion states. The anion “knows” it is a weakly bound attachment to a particular neutral
threshold. This consistency of \( f^{m,m} \) composition is true not only within the MCDF manifolds
of both anion and neutral, but also for all correlation configurations that do not attempt to
change the \( f \) occupancy (within the wavefunctions of the low-lying levels of interest).

Our approach was to extract dominant \( lsj \) terms for each element on a moderately sized
neutral calculation, freeze that smaller \( f^{m,m} \) set of terms, and use this simpler basis set
with the methodology discussed in Section 1.3.2.2 when pasting together all the correlation
configurations for the J-parity calculation of an anion or neutral. For 
attachment to 
thresholds, this is very straightforward since the 
composition is identical to the full 
configuration LSJ due to the closed 
subshell. For attachments to 
(neutral con-
figurations, it is a bit trickier since one needs to consider the 
terms within the 
group for each 
as they appear in the levels of interest in a range of total Js, but it is nonetheless a 
well-defined process. Once the methodology was well automated, this initial stage was the 
primary focus of the “human time” spent on each anion. Test calculations on the smaller 
evaluations did not converge. 
for each 

The second great realization was that the remaining 2- to 4-electron piece of the anion 
and neutral bases were also remarkably consistent from system to system despite changing 
and 
occupancy. This allowed us to tailor that piece of the bases on a simpler system 
such as 
and apply the same replacements with 
restrictions when performing the 
complex calculations such as 
. 
Finally, we also used the fact that the mathematics of piecing two groups of electrons 
together is essentially independent of the 
That is, the file that was used for 
for a given total 
would be identical to the same set of subshell 
such as 
. Together with other automation mentioned in Section 1.3.2.2, we were able to 
set up file naming conventions so that moving from one system to the next in the row was 
simplified to making a few global search-and-replace edits to the thousands-of-lines long 
program input files. 

Our results of the 3-paper lanthanide and actinide survey [2–4] are summarized in 
Table 1.1. The wealth of bound anion states is attributed, particularly on the left sides of 
each 
the many low-lying neutral thresholds over a wide range of Js due to the density of states arising from the 
group (compared to, say, a transition metal with no such group). Despite the fact that we have included few second-order effects, nor added any 
core-valence correlation, and frozen the occupancy of the core-like 
subshell for each calculation, the results seem consistent with experiment where applicable. For example, in the 
case, we re-evaluated our placement of anion 
manifolds by using the actual 
state rather than a simpler high-J excited state [41]. By using central Js we were comparing anion and neutral calculations with similar density of states (levels per eV) so any second-order type deficiencies in the basis sets that caused improper positioning of higher but near by excited levels tended to wash out between anion and neutral. The revised ab initio RCI electron affinity [3] was more consistent with the re-evaluation of the Davis and Thompson value [35] and that of Walter et al. [44]. A new measurement of the EA of 
has yielded a value of 570(20) meV [48]. 

At the other end of the lanthanide row, our prediction of the 
electron affinity of 22 meV is in reasonable agreement with the Nadeau et al. measurement of 32 meV [39]. In between, our results predict a linearly decreasing binding of 
attachments moving left to right across each row mimicking a similar linear relation long known for transition metal 
thresholds [49]. This trend that arises from our ab initio computations improves our confidence that experimenters searching for anion states in the middle of the rows would be well recommended to begin with our predictions. 

In addition to the linear relation of 
binding energies, our analysis showed a trend in 
attachments that produced an anion 
attachment on either side of each low-lying neutral