

Calculations of Nd⁻ binding energies and photodetachment partial cross sections

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The electron affinity for neodymium is determined from relativistic configuration interaction calculations to be 169 meV, and six additional bound excited states are also predicted. These $6p$ attachments to the $4f^4 6s^2$ neutral ground state configuration are carefully analyzed with respect to approximate LS total term and LSJ of the the $4f^4$ subgroup. This analysis is used to drastically reduce the basis size of the calculations and preselect channels for potentially large photodetachment partial cross sections. Estimations of the effects of the mixing of resonance states in the partial cross section calculations suggest that for incident photon energies ~ 2.0 eV or larger, $6s$ detachments to excited $4f^4 6s 6p$ thresholds will represent the dominant channels of the total cross section.

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I. INTRODUCTION

The Lanthanide negative ions have long been of interest to our group due to the level of complexity in calculations dealing with configurations with open shell $4f^n$ subgroups. The robustness of the relativistic configuration interaction (RCI) methodology is ideal for such complicated systems, where careful analysis of configurational energy contributions to multiple states is essential for the tailoring of basis sets to produce manageable calculations (our current bases are limited to 20 000 members [1]). For example, past negative ion RCI calculations [2, 3] have benefited greatly from the REDUCE methodology [4, 5], which performs a rotation of the basis members of a correlation configuration to maximize the number that have zero interaction with the Dirac-Fock (DF) configurations of interest (and can thus be removed from the basis).

Because of this complexity of the open $4f$ subshell (in some cases not yet fully collapsed), computational studies of negative ions have thus far been primarily relegated to the lower Z (La⁻ [6, 7], Ce⁻ [8, 9], and Pr⁻ [10]) or higher Z (Tm⁻ [11, 12], Yb⁻ [13–16], and Lu⁻ [15, 17, 18]) ends of the Lanthanides. In an overly optimistic period following the expansion of the main RCI program [1] from a basis size of 7000 to 20 000, we attempted to study $6p$ attachments to both the odd parity ground state and the extremely low lying [19] even parity first excited state of Tb. While preliminary results seemed promising [20], the problem ultimately proved too complex to acquire the desired level of accuracy with the restrictions that were required of the correlation configurations at the time (too many correlation losses with the REDUCE methodology and J restrictions of subgroups of electrons were unrecoverable). More recently, better results have been obtained in a study of long lived metastable states in Eu⁻ [21], where restrictions on the LS term of the half full $4f^7$ group were used to trim the RCI basis size by a factor of 25, nearly on par with the amount of reduction typically seen with the REDUCE [4, 5] procedure mentioned

above.

During the time that these computations have been performed, the experimental community has been studying Lanthanide negative ions with a variety of techniques, including laser excitation and accelerator mass spectrometry (AMS) [22–26], laser photodetachment electron spectroscopy (LPES) [27–33], and tunable laser photodetachment threshold spectroscopy (LPTS) [34]. To date, all the Lanthanide negative ions have been seen except for Pm⁻, Ho⁻, Er⁻, and Yb⁻, the last having been shown to be unbound [35].

Recently, we performed a detailed study of photodetachment partial cross sections of Ce⁻ [9]. The ground state of Ce⁻ was found to have the LS composition ($^4H_{7/2}$) of a $6s$ attachment to excited $4f5d^2 6s$ $^5H_{3,4}$ thresholds rather than a direct $5d$ attachment to the Ce $4f5d6s^2$ 1G_4 ground state. Partial cross section calculations verified that the $6s$ detachment channels to these excited thresholds were much stronger than $5d$ detachment to the ground state. A reinterpretation of earlier LPES measurements [30] with these considerations led to a reduction of the electron affinity (EA) of Ce⁻ from 0.955(26) eV [30] to ~ 0.660 eV [9]. Recent LPTS measurements [34] seem to corroborate this newer value.

With increased attention to Lanthanide negative ions in the experimental community, we would like to expand our capabilities to deal realistically with the more complicated systems in the center of the rare earth rows. Knowledge of ground state configurations, number of bound states, and LS composition of those states will be increasingly useful to experimenters as they improve their own methods. In particular, we would like to be able to predict in an *ab initio* fashion which types of detachments, e.g. $6s \rightarrow \epsilon p$ vs $6p \rightarrow \epsilon d$, are more likely to produce strong features in the experimental spectra in order to confirm RCI analyses with those of asymmetry parameter measurements of LPES experiments [33] and the near threshold behavior of LPTS experiments [34].

With these considerations in mind, the next logical

step is to forge one step further toward the center of the Lanthanides, keeping in mind the need for new techniques that will be required to retain reasonable basis sizes for even more complicated systems. Nd^- is a good candidate at this stage, since an experimental lower limit of 1.916 eV [33] provided by LPES measurements is available to compare to these *ab initio* RCI results.

II. COMPUTATIONAL METHODOLOGY

A. Radial Wavefunctions

Our one-electron radial wavefunctions are generated by Desclaux’s multiconfigurational Dirac-Fock (MCDF) program [36]. The even Nd radials are generated with three configurations, $4f^4(6s^2 + 5d^2 + 6p^2)$, while the odd cases are created with two, $4f^4(6s6p + 5d6p)$; both selections ensure that numerical $5d$ and $6p$ DF radial functions are present in the basis of each J -parity calculation. For the negative ion states the radials are generated using a three configuration MCDF calculation with the dominant configuration $4f^46s^26p$ and two largest (in terms of final RCI mixing) correlation configurations, $4f^45d6s6p$ and $4f^46p^3$. The latter is important for the binding of the $6p$ electron, since the presence of a portion of the MCDF wavefunction with multiple occupancy of the $6p$ subshells forces either the $6p_{1/2}$ or $6p_{3/2}$ radial wavefunction to converge to a bound solution (the effective charge Z^* is reduced gradually to its true value during a series of iterative steps).

In the case of Nd^- we noticed a large correction in some bound excited states to the $6p$ radial wavefunction (and to a lesser extent to $5d$) in the form of correlation configurations representing single replacements of the $6p$ electron. The cause is the difference in the $6p_{1/2}$ and $6p_{3/2}$ radial wavefunctions which, when optimized to a state that is primarily a $6p_{1/2}$ attachment, have average radii of ~ 7.5 and ~ 5.6 a.u., respectively (the opposite is true for a $6p_{3/2}$ attachment). This problem has been solved in Nd^- by swapping the more compact radials for each J with the more diffuse wavefunction from a calculation optimized to the other attachment (orthonormality is later ensured within the RCI calculation). The result is a negligible change in the energy of the lowest level of each J with ~ 0.4 eV improvement in the position of some excited states in a small MCDF calculation, minimizing the necessity of correlation effects to provide this correction.

B. RCI Basis Sets

Our RCI basis functions are constructed from Slater determinants of the one-electron wavefunctions, and each RCI wavefunction is an eigenstate of J , J_z , and parity. Subshells not present in the MCDF configurations are represented by screened hydrogenic functions, denoted

by vl and referred to as “virtual” orbitals. The effective charge, Z^* , of these functions is determined in the RCI process by energy minimization. The *ab initio* binding energies (BEs) are then determined by direct comparison of the total energies of separate RCI calculations of Nd^- and Nd with bases carefully constructed to contain the same types of correlation (single and double replacements relative to the DF configurations) and the same amount saturation of the basis set (number of virtual orbitals of each l).

Typically, for an EA study we would like to include exclusion effects involving correlation configurations representing core and core-valence single and double replacements. For example, replacements of the form $5p6p \rightarrow vl^2 + vlvl'$ are present only in the negative ion, but replacements like $5p \rightarrow 6p$ or $5p^2 \rightarrow 6p^2$ tend to favor the neutral atom, since the $6p$ subshells is already singly occupied in the DF configuration of the negative ion. However, opening the core in this manner can be disruptive to the contributions of the valence correlation configurations, since it can preferentially introduce several eV of correlation energy to the MCDF configurations, compared to the ~ 1 eV valence correlation already present. The alteration in the relative position and mixing coefficients of nearby valence configurations can produce a subsequent loss of correlation energy of 20% or more for some configurations, countering any exclusion effects that are introduced by opening the core. The same is also true for the $4f^4$ subgroup; the single replacement $4f \rightarrow vf$ can provide an effective correction to excited states of a given J on the order of 10–15 meV within a manifold (where the $4f$ is optimized to the lowest level of that J) or as much as ~ 100 meV for configurations different from that of the lowest level. However, continuing the process with $4f^2$ double replacements results in several eV correlation to the DF configuration, again disrupting the mixing and correlation energy of valence configurations. These effects can be mitigated somewhat by careful restriction of the LSJ of subgroups of electrons. For example, with the single replacement $5p \rightarrow vp$, the resulting $5p^5vp$ subgroup can be restricted to the 1S_0 term to ensure that only the correction to the $5p$ radial wavefunction is being introduced (e.g. unrestricted $5p \rightarrow vp$ in the $4f^46s^26p_{3/2}$ basis members is effectively a core-valence double replacement for the $4f^46s^26p_{1/2}$ basis members).

When dealing with Lanthanides there is also the complication of relative position and treatment of manifolds containing $4f^n$ vs $4f^{n-1}$ subgroups. The differing number of $4f$ electrons partially screening one another and the reverse difference of valence electrons outside the $4f$ shell results in very different optimization of these subshells in the MCDF calculation [36]. In Nd and Nd^- the $4f$ radial wavefunctions have average radii of ~ 1.01 a.u. and ~ 0.95 a.u. when optimized to configurations with $4f^4$ and $4f^3$ subgroups, respectively (the corresponding one electron energies are ~ 0.43 a.u. and ~ 0.73 a.u.). The effect seen in our RCI calculations is an error in relative position of over 1.0 eV when the $4f$ radial is not corrected

by inclusion of $4f \rightarrow vf + vf'$ single replacements. Including these corrections, however, in $4f^3$ configurations would introduce effective $4f^2$ double replacements to $4f^4$ configurations, again disrupting the relative positions of valence correlation configurations by several eV. Fortunately, we have found negligible mixing of the $4f^3 5d 6s 6p$ configuration (levels starting at $\sim 20\,000\text{ cm}^{-1}$ [19]) or other $4f^3$ configurations into the $4f^4 6s^2$ Nd even states, even when the diagonal elements of the RCI Hamiltonian matrix are artificially shifted to move these levels to their experimental energies. Similar $4f^3$ correlation configurations were found to have negligible (few meV) impact on the $4f^4 6s^2 6p$ Nd⁻ states. In the Nd odd states we have made intermediate calculations to determine the effects of the $4f$ corrections mentioned above to the various LS terms of the $4f^3(5d+6s)^3$ configurations. In the final odd parity calculations the diagonal elements of these basis functions are then differentially shifted an amount relative to the expected corrections to gain best agreement with experimental positioning [19] of these levels. This allows the production of a semi-empirical energy spectrum without the difficulties of introducing correlation configurations with $4f^2$ subgroups (and four other valence electrons), which would be particularly complicated numerically (many times more determinants and basis functions than, for example, $4f^3 5d^2 6s$). Ultimately, the impact here is on the relative purity of $4f^4 6s 6p$ thresholds of the partial cross section calculations (see Sec. IID).

Many of the intermediate calculations testing the above difficulties have pushed the limits of the current RCI code in the Nd⁻ case. For example, a redimensioning to allow >1 M total determinants was required for the first time. Even so, these largest calculations typically take 4–6 hours (with the additional simplifications discussed in Sec. IIC and the LSJ restrictions mentioned above) on a PC with a 2.4 GHz AMD 64-bit processor. While not prohibitive to include, these competing exclusion effects between negative ion and neutral states in these cases were found to affect the BEs only by ~ 10 meV. This does not take into account, however, possible effects from unrestricted core-core and core-valence correlation which is simply too difficult to include at this juncture (the required triple and quadruple second order replacements that would simultaneously restore lost contributions from valence configurations would certainly require several times the basis size and maximum total determinants).

Finally, we have noted that for Nd⁻ and Nd all the configurations of interest have valence electrons (if $4f$ is considered core-like) with a maximum $l = 1$: $4f^4 6s^2 6p$, $4f^4 6s^2$, and $4f^4 6s 6p$. Perhaps not surprisingly, the contributions to the RCI correlated energy from configurations containing vg electrons were found to be negligible (a few meV). Replacements such as $5d 6p \rightarrow vfvg$, for example, would be more important in a configuration with a $5d$ electron than $6s^2 \rightarrow vg^2$ is in these DF configurations. This fact may be of much greater significance

as we move on to more difficult Lanthanides since we will likely be attaching $6p$ electrons to $4f^n 6s^2$ configurations there as well (the Gd $4f^7 5d 6s^2$ ground state and the aforementioned $4f^8 5d 6s^2$ lowest excited state of Tb being the obvious exceptions). The ability to restrict virtual subshells to $l \leq 3$ with negligible loss of correlation will significantly limit the size of the RCI bases required for these systems.

C. LS Basis Functions and Subgroups

The RCI methodology is entirely relativistic, but we do have the capability of producing approximate LS basis functions through a simple rotation of the $j - j$ basis. The $j = l - 1/2$ and $j = l + 1/2$ radial wavefunctions for a given nl subshell are treated as equivalent and the major component is treated as a nonrelativistic spinor (the minor component is neglected). The LS approximate eigenstates are then created by diagonalizing the $L^2 + S^2$ matrix using these criteria. In the case of Nd⁻, two separate calculations are then performed; one with these LS basis functions and one with the original $j - j$ basis to determine the J of the $4f^4 6s^2$ core portion of the wavefunction and the j of the attached $6p$ electron.

In order to begin building an RCI basis set with a system as complex as Nd⁻, we have made one principle approximation not mentioned in Sec. IIB. That is to fix the LS term of the $4f^4$ and $4f^3$ electron subgroups throughout the calculations. Note that all of the levels of interest here have terms of 5I and 4I [19] for these subgroups (there are a few levels with terms of 5F and 4F below $20\,000\text{ cm}^{-1}$ [19], and our DF level calculations place the $4f^4 6s^2\ ^3H$ manifold at about $15\,000\text{ cm}^{-1}$). Comparisons of DF calculations including all the LS terms of the $4f^4$ subgroups for the negative ion states and neutral thresholds and those with only 5I show a loss in energies of < 40 meV. The relative changes in the BEs, however, are ~ 2 meV, so the purity of the LS term can be used to our advantage using one caveat; we must keep track of the core portion of the negative ion states as described above. The $4f^4 6s^2\ ^5I_4$ ground state is slightly less pure than 5I_5 (1.4% vs 0.8% 3H), resulting in differing changes in energy with this single term approximation (38 meV vs 20 meV). It is by weighting the binding energies of negative ion states by their attachment analysis that we arrive at the ~ 2 meV figure. The savings of this approximation in number of determinants is only a few percent, since almost all the $4f^4$ determinants are needed to create 5I due to its high L , but the number of basis members themselves is reduced by a much greater degree since there is only one 5I basis function per J of this subgroup (c.f. four for 3H , three for 3G , etc.). The reductions for $4f^4$ $J = 4, 5, 6, 7,$ and 8 are factors of 19, 14, 13, 7, and 7, respectively, so depending on the rest of the valence configuration and the total J of the calculation the typical reduction in the basis size for each configuration is ~ 15 . Without this approximation (and assuming other

techniques such as REDUCE were not used) each RCI calculation of 5–6000 basis functions would then be approximately four times the current code limit of 20 000 [1]. Even if the code could be updated to accommodate the size, the calculation would be scaled up from 4–6 hours to several weeks of CPU time for a gain of $\sim 1\%$ accuracy in the wavefunction.

The method of preparing the external data required to generate LS eigenstates for every basis function (or in this case on a subgroup of every basis function) has been greatly improved over the approach in the Eu^- work [21]. There each configuration was separately created in its entirety, even though the $4f^7$ subgroup was consistently generated with two terms (8S and 6P). The RCI code contains options for piecing together two subgroups via angular momentum addition:

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

though the algorithm performs the process on a single relativistic configuration at a time, precluding the rotation to an LS basis described above.

With Nd^- , a single correlation configurations can have $>10\,000$ determinants (this is even taking into account only the relativistic configuration of the valence electron, e.g. $4f^4({}^5I)5d_{5/2}6p_{3/2}vd_{5/2}$). In general, the creation of input data of that size takes approximately the same time as a complete RCI calculation with a similar number of basis functions, and a series of full configuration preparations may become 5 days worth of CPU plus user time for each J -parity combination, depending on the desired amount of correlation. With this in mind a separate angular momentum addition code has been implemented. In this case, basis functions for each subgroup j are created separately along with determinantal information for each m , generated with the step down operator. The code then performs the addition of all the possible combinations, e.g. 5I $j = 4-8$ with $5d_{5/2}6p_{3/2}vd_{5/2}$ $j = 1/2-13/2$ (or fewer if j restrictions are desired), that make the desired total J . The preparation time (CPU) of the individual pieces is a few seconds per file, while the addition is performed in about a minute for the example above, compared to ~ 2 hours required to diagonalize the entire configuration at once using the prior method. In addition, the switch to another total J is a trivial change of a single variable, so the complete input data for each additional J is generated in ~ 10 minutes (opposed to the several days mentioned previously). Similarly, the prepared valence electron data can be easily ported to the next project where a new $4f^n$ LS term is all that is required (in fact, in this case three-electron files are reused between $4f^4$ configurations in Nd^- and $4f^3$ configurations in the odd Nd neutral calculations).

D. Partial Cross Sections

Partial cross section calculations were performed for both $6p$ detachment (to the Nd $4f^46s^2$ ground state thresholds) and $6s$ detachment (to $4f^46s6p$ excited state thresholds which begin at $\sim 14\,000$ cm^{-1} [19] in the neutral spectrum). Test calculations indicate that $\sim 8\%$ mixing of $4f^45d6s6p$ in the Nd^- states is insufficient to produce reasonably large partial cross sections ($>1\%$ of the ground state channels) for $6p$ detachment to $4f^45d6s$ excited states. Potential $4f$ detachments to odd Nd $4f^3(5d+6s)^2$ thresholds were found to be at most four orders of magnitude weaker than the the ground state to ground state channels.

The continuum radial wavefunctions are created using the relativistic continuum wave solver code of Perger *et al.* [37, 38]. Recently, we have updated this code to allow up to 1000 basis functions for the neutral core, with coefficients determined by the neutral RCI calculations. The previous version required only a single dominant basis function from the DF configuration, which produced difficulties with treating orthogonality of DF and ϵl radial wavefunctions (e.g. $4f^46s6p\epsilon p$ now contains both $6p_{1/2}$ and $6p_{3/2}$, so the continuum function is properly orthogonal regardless of the j of ϵp). The neutral atom plus continuum wavefunctions are created by an angular momentum addition algorithm similar to the one discussed in Sec. II C using the frozen core approximation. A new data preparation code was implemented to prepare files for this program as well as the relativistic cross section program. Its capabilities are such that data for hundreds of individual channels can now be processed in a few minutes, primarily from a single 30–40 line input file.

The cross section calculations themselves are performed on smaller RCI wavefunctions than are used in the final BE calculations. The bases were carefully trimmed to $\sim 300\,000$ total determinants with as little loss of correlation as possible by using one set of virtual orbitals rather than two and retaining only those configurations with 0.01% weight or greater. The simplifications were made to allow reasonable computation times for each individual channel of the order of 15 minutes or less, whereas use of the full RCI BE wavefunctions would be prohibitively expensive; ~ 10 hours each for hundreds of channels. The impact of resonances was explored using Fano's theory [39] mixing only a single channel and resonance at a time. An expansion of our methodology to a more thorough treatment of multiple channels with multiple resonance coupling as described by Mies [40] will be left to a less computationally complex system. Our goal with these calculations is not extreme accuracy, but rather an indication of the order of the relative strength of the $6p$ and $6s$ detachments for comparison with the LPES result [33].

The final set of cross section calculations is made using several considerations of the one-electron dipole operator ($\Delta L = \pm 1$ or 0, $\Delta S = 0$, and $\Delta J = \pm 1$ or 0) to limit

the necessary number of channels. For example, a Nd- $4f^46s^26p$ state with $j - j$ composition of >90% attachment to 5I_4 will have negligible partial cross section for channels with the 5I_5 final state threshold. Likewise, a state that is primarily a $6p_{1/2}$ attachment will have a weak $6p$ detachment to $\varepsilon d_{5/2}$. The $6s$ detachments are less straightforward, but considering that the $6s \rightarrow \varepsilon p$ “carries” the selection rules, the remaining portion of the Nd $^-$ configuration must match the neutral threshold. For a Nd $^-$ state with a fairly pure LSJ composition, the corresponding $4f^46s6p$ Nd thresholds with large cross sections have $L' = L$, $S' = S \pm 1/2$, and $J' = J \pm 1/2$ (e.g. $^6K_{9/2} \rightarrow ^5K_5 + ^7K_{4,5}$).

III. RESULTS

A. Binding Energies

LS composition and attachment analysis for seven bound states of Nd $^-$ are presented in Table I. An additional five states that are unbound by less than 100 meV relative to the Nd $4f^46s^2 ^5I_4$ ground state are also presented. These additional levels are bound relative to the 5I_5 first excited state (~ 140 meV [19]), and they are presented here in the event that future experimental studies that identify specific channels suggest further binding that is absent from these *ab initio* RCI calculations (c.f. Sec. II B and II C for the approximations made to accommodate the complexity of this system). The expectation is that missing core-core and core-valence correlation or configurations representing replacements from the $4f^4$ subgroup may have a differential effect between Nd $^-$ and Nd calculations (i.e. the EA), but they are unlikely to create significant changes in position among the Nd $^-$ $4f^46s^26p$ states or in their LS composition.

The neutral $4f^46s^2$ RCI wavefunctions were found to have mixing of the $4f^46p^2$ and $4f^45d^2$ configurations of $\sim 6.7\%$ and $\sim 0.7\%$, respectively, with essentially no mixing with the $4f^45d6s$ manifold. The Nd $^-$ states have RCI mixing for the $4f^45d6s6p$, $4f^46p^3$, and $4f^45d^26p$ configurations of 7.0–8.0%, 3.0–3.5%, and $\sim 2.0\%$, respectively. The large mixing of $4f^45d6s6p$ is not generally of the form of $6p$ attachments to $4f^45d6s$ states (which would beg the question why $6s \rightarrow 5d$ is important in Nd $^-$ but not in Nd) but rather as double replacements such as $6s6p_{1/2} \rightarrow 5d_{5/2}6p_{3/2}$.

B. Partial Cross Sections

The partial cross sections presented in Table II were calculated using the *ab initio* RCI BE of Table I and an incident photon energy of 2.41 eV (a typical energy used in LPES experiments [30]). LS designations for some of the $4f^46s6p$ thresholds are estimated by comparing approximate RCI energy position and Landé g values of

levels with no experimental LS designation [19]. A summation of individual channels is made for each negative ion state and neutral core threshold combination, with the data presented here as relative to this ground state to ground state pair. For each detachment we consider mixing of the final neutral plus continuum wavefunction with potentially large resonance states, e.g. those of the form $6s \rightarrow 6p$ and $6p \rightarrow 5d + 6s$, which are placed relative to the neutral $4f^46s6p$ and $4f^45d6s$ manifolds using the same methods as the bound state $6p$ attachments to $4f^46s^2$. As mentioned previously, the full coupling of multiple channels and resonances using the Mies theory [40] has been considered prohibitively expensive at this stage of the development of our methodology. We do, however, attempt to provide a conservative estimate to the effects of resonances by including the resonance impact for just one of the individual channels that make up each entry, albeit the largest of the group. In cases where the RCI placement of these resonances is very close to the energy of the neutral plus continuum wavefunction energy (due to the chosen photon energy and perhaps the accuracy of the calculations) a minimum energy difference of 0.25 eV is imposed to avoid artificially inflating the mixing of the resonance state.

The important point of Table II is that while, in general, one expects a larger cross section for detachment of the much more diffuse $6p$ electron, the fact that the $6s$ detachments are much closer to threshold (for photon energies of 2.0–2.5 eV) results in calculated partial cross sections of approximately the same strength. Additionally, $4f^46s6p^2$ resonance states that are effectively $6p$ attachments to higher $4f^46s6p$ neutral thresholds may increase these $6s$ detachment cross sections as much as two orders of magnitude, while the $6p$ detachments are only affected by resonances by approximately a factor of two. Ultimately, these results suggest that to study the true ground state to ground state photodetachment channels, experimenters may need to use photon energies below ~ 1.7 eV [19] to avoid these $4f^46s6p$ thresholds completely.

IV. CONCLUSIONS

Treatment of the $4f^n$ subgroup in Lanthanide negative ion states as core-like electrons with fixed LS terms is a viable approach to the computational complexity of these systems. While accuracy of the EA relative to the neutral ground states may suffer somewhat due to these approximations, we expect that the composition of these negative ion states and their relative positions should be relatively unaffected.

The composition of these levels can be used in tandem with experimental results to identify spectral features and obtain better estimates of the EA. For example, using our *ab initio* BEs, we note that the Nd $^-$ $^6K_{9/2}$ ground state has strong detachment channels to $^7K_{4,5}$ Nd thresholds with energy differences of 1.864 and 1.944 eV

TABLE I: Binding energies (in meV) for $\text{Nd}^- 4f^4 6s^2 6p$ states (relative to the $4f^4 6s^2 {}^5I_4$ neutral ground state), grouped by total J . The LS and attachment analyses are presented as percentages of composition within the DF configuration. States with negative binding energies presented here lie above the neutral ground state given the approximations made for these *ab initio* RCI calculations, though each is bound relative to its natural threshold (5I_5 lies ~ 140 meV [19] above the Nd ground state).

LS Composition	Attachment Analysis	BE
${}^6H_{5/2}$ 100	${}^5I_4+6p_{3/2}$ 100	86
${}^4H_{7/2}$ 49, 6I 43, 6H 8	${}^5I_4+6p_{1/2}$ 100	144
${}^6I_{7/2}$ 49, 6H 33, 4I 18	${}^5I_4+6p_{3/2}$ 100	76
${}^6H_{7/2}$ 59, 4H 33, 6I 8	${}^5I_5+6p_{3/2}$ 100	-70
${}^6K_{9/2}$ 89, 4I 10, 4H 1	${}^5I_4+6p_{1/2}$ 94, ${}^5I_4+6p_{3/2}$ 5, ${}^5I_5+6p_{3/2}$ 1	169
${}^4I_{9/2}$ 47, 6I 40, 6K 6, 6H 5, 4H 2	${}^5I_4+6p_{3/2}$ 94, ${}^5I_4+6p_{1/2}$ 5, ${}^5I_5+6p_{3/2}$ 1	66
${}^4H_{9/2}$ 42, 6I 31, 6H 23, 4I 3, 6K 1	${}^5I_5+6p_{1/2}$ 99, ${}^5I_4+6p_{1/2}$ 1	-3
${}^4I_{9/2}$ 37, 6H 35, 6I 23, 4H 3, 6K 2	${}^5I_5+6p_{3/2}$ 98, ${}^5I_5+6p_{1/2}$ 1, ${}^5I_4+6p_{3/2}$ 1	-77
${}^6K_{11/2}$ 60, 4K 38, 6I 2	${}^5I_4+6p_{3/2}$ 86, ${}^5I_5+6p_{1/2}$ 13, ${}^5I_5+6p_{3/2}$ 1	81
${}^4K_{11/2}$ 43, 6K 33, 4I 18, 6I 4, 6H 1, 4H 1	${}^5I_5+6p_{1/2}$ 85, ${}^5I_4+6p_{3/2}$ 13, ${}^5I_5+6p_{3/2}$ 2	6
${}^6I_{11/2}$ 52, 4I 21, 4K 16, 6H 6, 6K 4, 4H 1	${}^5I_5+6p_{3/2}$ 97, ${}^5I_5+6p_{1/2}$ 2, ${}^5I_6+6p_{3/2}$ 1	-76
${}^6K_{13/2}$ 69, 4K 27, 6I 3, 4I 1,	${}^5I_5+6p_{3/2}$ 94, ${}^5I_6+6p_{1/2}$ 6	-56

(the average is perhaps fortuitously close to the experimental EA of 1.916 eV [33]). If, however, this 1.916 eV [33] value is specifically identified with the ${}^6K_{9/2} \rightarrow {}^7K_4$ channels, the implication would be that the RCI BEs presented here should be uniformly increased by 0.052 eV.

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TABLE II: Photodetachment partial cross sections relative to the sum over the channels representing $6p$ detachments from the $\text{Nd}^- 4f^4 6s^2 6p \ ^6K_{9/2}$ ground state to the $\text{Nd} 4f^4 6s^2 \ ^5I_4$ ground state. The effect of resonances (in the “ $\sigma(+R)$ ” column) is estimated from calculations that mix a single channel with a single resonance. Terms in parentheses represent secondary LS terms from the compositional analysis that also contribute to the cross section.

6s detachments: $4f^4 6s^2 6p \rightarrow 4f^4 6s 6p \ \varepsilon p$				
Nd^-	Nd	ΔE (eV)	σ	$\sigma(+R)$
$^6K_{11/2}(^4K)$	$^5K_6(^3K)$	2.281	0.1	5.7
$^4K_{11/2}(^6K)$	$^5K_6(^3K)$	2.207	0.1	5.0
$^6K_{9/2}$	5K_5	2.094	0.1	32.8
$^4H_{7/2}$	$^7H_3(^5H)$	2.064	0.1	33.2
$^6I_{7/2}(^6H)$	$^5I_4(^5H)$	2.025	0.1	36.9
$^6H_{5/2}$	$^7H_3(^5H)$	2.006	0.3	48.0
$^6H_{5/2}$	7H_2	1.993	0.6	20.9
$^4H_{7/2}(^6I)$	$^5H_4(^7I)$	1.979	0.4	32.2
$^6K_{11/2}(^4K)$	$^7K_6(^5K)$	1.968	0.4	4.8
$^6I_{7/2}(^6H)$	$^7I_4(^7H)$	1.965	0.4	24.6
$^4I_{9/2}(^6I)$	7I_4	1.955	0.3	4.2
$^6K_{9/2}$	$^7K_5(^5K)$	1.944	0.3	29.1
$^4H_{7/2}(^6I)$	$^7I_3(^5H)$	1.934	0.3	33.1
$^4K_{11/2}(^6K)$	5K_5	1.931	0.3	14.2
$^6I_{7/2}(^6H)$	$^5H_4(^7I)$	1.911	0.1	23.8
$^4K_{11/2}(^6K)$	$^7K_6(^5K)$	1.894	0.1	4.7
$^6I_{7/2}(^6H)$	$^7I_3(^5H)$	1.866	0.3	15.7
$^6K_{9/2}$	7K_4	1.864	0.6	40.0
$^6K_{11/2}(^4K)$	$^7K_5(^5K)$	1.855	0.3	7.0
$^4K_{11/2}(^6K)$	$^7K_5(^5K)$	1.781	0.1	1.9
6p detachments: $4f^4 6s^2 6p \rightarrow 4f^4 6s^2 (\varepsilon s + \varepsilon d)$				
Nd^-	Nd	ΔE (eV)	σ	$\sigma(+R)$
$^6K_{9/2}$	5I_4	0.169	1.0	2.2
$^4K_{11/2}(^6K)$	5I_5	0.146	0.5	0.6
$^4H_{7/2}(^6I)$	5I_4	0.144	0.8	1.8
$^6H_{5/2}$	5I_4	0.086	0.9	1.4
$^6K_{11/2}(^4K)$	5I_4	0.081	0.6	0.9
$^6I_{7/2}(^6H)$	5I_4	0.076	1.0	2.3
$^4I_{9/2}(^6I)$	5I_4	0.066	0.9	1.5

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