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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 of the total configuration and LSJ of 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 $4f^4 6s6p$ 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 program [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 [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., $6s \rightarrow \varepsilon p$ vs $6p \rightarrow \varepsilon d$, 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. Multiconfigurational Dirac-Fock radial wave functions

Our one-electron radial wave functions are generated by Desclaux's multiconfigurational Dirac-Fock (MCDF) program [36]. Both neutral and negative ion radials are generated with multiple configurations to ensure that numerical $5d$ and $6p$ DF radial functions are present in the basis of each J-parity calculation. In the negative ion cases, the $6p$ radial wave function corresponding to the dominant attachment for each state is found to be much more diffuse than its counterpart (average radius ~7.5 vs ~5.6 a.u.). In order to simultaneously optimize our radial wave functions to both $6p_{1/2}$ and $6p_{3/2}$ attachments, our basis sets are selected to use the more diffuse radial wave functions from two separate calculations, e.g., those optimized to the lowest roots of both $J=9/2$ and $J=11/2$ which are $6p_{1/2}$ and $6p_{3/2}$ attachments to the Nd ground state, respectively. A similar swapping of the more diffuse $5d$ radial functions (present in the $4f^4 5d6s6p$ correlation configuration) is also performed between MCDF radial bases.

B. RCI basis sets

Our RCI basis functions are constructed from Slater determinants of the one-electron wave functions, and each RCI wave function 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 of saturation of the basis set (number of virtual orbitals of each l).

The most difficult stage of a typical RCI EA study is determination of the appropriate extent to which the shallow core should be opened. Addition of several eV correlation energy can easily disturb the much smaller contributions from valence configurations as they are artificially "pulled away" from the DF manifolds, resulting in decreases in their CI mixing coefficients. The corresponding loss in correlation energy (typically as large as 20%) must be regained by careful inclusion of the same type of core-core and core-valence correlation in the "problem" configurations as was introduced to the DF configurations. These second-order effects in the form of complicated triple and quadruple replacements with respect to the DF configurations can often represent the bulk of the RCI basis. Additionally, because there are competing exclusion effects, such as $5p^2 \rightarrow 6p^2$ (which favors the neutral relative to a $6p$ negative ion attachment) and $5p6p \rightarrow vl^2$ (present only in the $6p$ negative ion attachment and not in the neutral calculation), the addition of several eV of correlation due to the opening of the core may ultimately result in only a few tens of meV differential correlation between the neutral and negative ion RCI energies. Given these difficulties and considering the desired extension of the methods presented here to more computationally difficult lanthanides in the future, we have elected to forgo opening the shallow core ($5s^2 5p^6$) in these calculations. The expectation is that any errors introduced by this restriction of the methodology will affect all the states of a given negative ion approximately equally, resulting in a common shift in the BEs with negligible effects on the mixing of LS terms and relative positioning of these states.

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]. Here we have treated the $4f$ subshell as essentially corelike, excluding correlation involving the $4f^4$ subgroup except where it is naturally present in our neutral Nd odd states in the form of the low-lying $4f^3(5d+6s)^3$ manifolds and those correlation configurations representing valence replacements with respect to these DF configurations. These neutral calculations are performed using DF radial bases optimized to the $4f^4 6s6p$ configurations, and errors in positioning of the levels containing $4f^3$ subgroups are corrected in a semiempirical manner by shifting their diagonal Hamiltonian elements to match the relative experimental position [19] of these manifolds. Ultimately, the impact here is on the relative purity of $4f^4 6s6p$ thresholds of the partial cross-section calculations (see Sec. II D). Fortuitously, we have found negligible mixing of the $4f^3 5d6s6p$ configuration (levels starting at ~20 000 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.

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 wave functions 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 wave function 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. II B. 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 cm^{-1} [19], and our DF level calculations place the $4f^4 6s^2$ ^3H manifold at about 15 000 cm^{-1}). Comparisons of DF calculations including all

TABLE I. Binding energies (in meV) for Nd$^-$ $4f^46s^26p$ states (relative to the $4f^46s^2$ $^5I_4$ 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 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 $4f^46s^2$ $^5I_4$ 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 (cf. 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 4 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 h to several weeks of CPU time for a gain of ∼1% accuracy in the wave function.

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,

$$|JM\rangle = (-1)^{j_1-j_2-M}\sqrt{2J+1}\sum_{m_1,m_2}\begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix}|j_1m_1,j_2m_2\rangle,$$

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 configuration 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) 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 ground-state to ground-state channels.

The continuum radial wave functions 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 neutral atom plus continuum wave functions are created by an angular momentum addition algorithm similar to the one discussed in Sec. II C using the frozen core approximation. A 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 wave functions 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 min or less, whereas use of the full RCI BE wave functions would be prohibitively expensive; $\sim$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 results [33].

The final set of cross-section calculations is made using several considerations of the one-electron dipole operator ($\Delta L=\pm1$ or 0, $\Delta S=0$, and $\Delta J=\pm1$ 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 $L'=L$, $S'=S\pm1/2$, and $J'=J\pm1/2$ (e.g., $^6K_{9/2}\rightarrow{}^5K_5+{}^7K_{4,5}$).

TABLE II. Photodetachment partial cross sections relative to the sum over the channels representing $6p$ detachments from the Nd$^-$ $4f^46s^26p$ $^6K_{9/2}$ ground state to the Nd $4f^46s^2$ $^5I_4$ 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.

Nd$^-$	Nd	ΔE (eV)	σ	$\sigma(+R)$
$6s$ detachments $4f^46s^26p\rightarrow4f^46s6p\varepsilon p$				
$^6K_{11/2}(^4K)$	$^5K_6(^3K)$	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
$^6K_{9/2}$	$^7I_5(^5K)$	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 $4f^46s^26p\rightarrow4f^46s^2(\varepsilon s+\varepsilon d)$				
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

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 $4f^4 6s^2$ $^5I_4$ ground state are also presented. These additional levels are bound relative to the $^5I_5$ first excited state ($\sim$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 (cf. Secs. 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$^-$ $4f^4 6s^2 6p$ states or in their *LS* composition.

The neutral $4f^4 6s^2$ RCI wave functions were found to have mixing of the $4f^4 6p^2$ and $4f^4 5d^2$ configurations of $\sim$6.7% and $\sim$0.7%, respectively, with essentially no mixing with the $4f^4 5d6s$ manifold. The Nd$^-$ states have RCI mixing for the $4f^4 5d6s6p$, $4f^4 6p^3$, and $4f^4 5d^2 6p$ configurations of 7.0%–8.0%, 3.0%–3.5%, and $\sim$2.0%, respectively. The large mixing of $4f^4 5d6s6p$ is not generally of the form of $6p$ attachments to $4f^4 5d6s$ 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 $4f^4 6s6p$ 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 wave function 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 $4f^4 6s6p$ and $4f^4 5d6s$ manifolds using the same methods as the bound state $6p$ attachments to $4f^4 6s^2$. 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 wave-function 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, $4f^4 6s6p^2$ resonance states that are effectively $6p$ attachments to higher $4f^4 6s6p$ 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 2. Ultimately, these results suggest that to study the true ground-state to ground-state photodetachment channels, experimenters may need to use photon energies below $\sim$1.7 eV [19] to avoid these $4f^4 6s6p$ thresholds completely.

IV. CONCLUSIONS

Treatment of the $4f^n$ subgroup in lanthanide negative ion states as corelike 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 effects on the composition of these negative ion states and their relative positions should be minimal.

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 (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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