Quasi-Atomic Bond Analyses in the Sixth Period: I. Relativistic Accurate Atomic Minimal Basis Sets for the Elements Cesium to Radon

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Disciplines
Physical Chemistry
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Relativistic Accurate Atomic Minimal Basis Sets for the Elements Cesium to Radon

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Abstract

Full-valence relativistic accurate atomic minimal basis set (AAMBS) orbitals are developed for the 6th row elements from cesium to radon, including the lanthanides. Saturated primitive atomic basis sets are developed and subsequently used to form the AAMBS orbitals. By virtue of the use of a saturated basis, properties computed based on the AAMBS orbitals are basis set independent. In molecules, the AAMBS orbitals can be used to construct valence virtual orbitals (VVOs) that provide chemically meaningful ab initio LUMOs with basis set independent orbital energies. The optimized occupied molecular orbitals complemented with the VVOs form a set of full valence molecular orbitals. They can be transformed into a set of oriented quasi-atomic orbitals (QUAOs) that provide information on intramolecular bonding via an intrinsic density analysis. In the present work, the development of the AAMBS for the sixth row is presented.

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1. Introduction

Orbitals are a fundamental concept that is indispensable to a chemist’s understanding of the behavior of chemical systems.\textsuperscript{1,2} Notably, the idea that atomic orbitals (AOs) combine to form molecular orbitals (MOs) is key to modern interpretations of chemical bonding. For instance, in computational chemistry, molecular orbitals are conceived as linear combinations of atomic orbitals (LCAO-MOs) when guessing initial approximations to molecular wave functions.

Optimization of a Hartree-Fock wave function through energy minimization results in well-defined occupied molecular orbitals. However, the unoccupied orbitals have nebulous meaning as they are mixtures of correlating functions, polarizing functions, Rydberg states, etc. that are composed of the remaining basis functions. The virtual orbitals are thus basis set dependent and only constrained by the orthogonality to the occupied orbitals. Yet many accurate electronic structure methods require the judicious choice of initial guess orbitals consisting of both occupied and unoccupied orbitals. Thus, there have been numerous efforts to produce modified virtual orbitals that are chemically meaningful, such as the improved virtual orbitals (IVOs),\textsuperscript{3} the averaged virtual orbitals (AVOs),\textsuperscript{4} and the modified virtual orbitals (MVOs).\textsuperscript{5} These methods are based on pseudo-exchange operators or pseudo-Fock operators in the canonical virtual orbital space.\textsuperscript{6,7} Alternatively, post-Hartree Fock methods such as second order perturbation theory (MP2)\textsuperscript{8} or singles and doubles configuration interaction (CISD)\textsuperscript{9-11} have been used to obtain LUMO-like orbitals by diagonalization of the density matrix, although such orbitals are obtained at an increased computational cost due to the use of at least double excitations in the correlated methods.
An alternative approach pursued by the present authors is based on the observation that the dominant part of a molecular wave function typically lies in the valence space, i.e., in the configuration space that is generated by the molecule-adapted minimal-basis-set orbitals of the atoms. This orbital space is considered the *internal* orbital space of the molecule, and the objective of the approach is to determine orbitals that provide effective bases for the internal space. This objective is achieved by extracting, from the occupied and virtual spaces of a molecular calculation, orbitals with maximal atomic-like character by a projective procedure that makes use of accurate atomic minimal basis set (AAMBS) orbitals of the free atoms. The procedure generates two types of orbitals: valence virtual orbitals (VVOs) and oriented quasi-atomic orbitals (QUAOs). The VVOs are certain orbitals in the virtual space that complement the optimized occupied orbitals so that these two orbital sets together provide a full minimal basis set (MBS) in the molecular valence space. The VVOs are obtained by computing overlaps of the unoccupied virtual orbitals with all orthogonalized AAMBS orbitals. This rectangular overlap matrix is diagonalized via a singular value decomposition (SVD) which produces the VVOs that, together with the occupied orbitals, form a full set of molecular MBS orbitals. It has been shown that performing a full configuration interaction calculation in this valence orbital space typically recovers approximately 80-90% of the internal correlation energy. In fact, the resulting VVOs are molecular orbitals that include the basis set independent *ab initio* realization of the LUMO concept. In all molecules examined so far, it has furthermore been found that the internal molecular orbital space obtained in the described manner can be spanned by orbitals that are very similar to orbitals of the free atoms, i.e., the orbitals in the internal orbital space can be transformed into atomic-like quasi-atomic orbitals (QUAOs). Therefore, this
representation also provides a basis for interpreting bonding in terms of interactions between atoms. Details of this bonding analysis are elaborated in the subsequent paper.

In order to perform such analyses, it is manifestly essential that highly accurate AAMBS are available. For all atoms from lithium to xenon, these orbitals were determined in previous publications excluding\textsuperscript{14} and including\textsuperscript{15} relativistic effects. In the present work, the relativistic AAMBS orbitals for all atoms from cesium to radon are developed including the lanthanides. To ensure the basis set independence of the resulting VVOs and QUAOs, saturated primitive basis sets are optimized and then used to compute the AAMBS orbitals. The determination of the primitive basis sets is discussed in Section 2. The expansions of the AAMBS in terms of the primitives are discussed in Section 3. A summary is given in Section 4. All numerical data has been stored to be freely available as described below.\textsuperscript{21} This data may also prove useful in other contexts.\textsuperscript{22} The usefulness of the AAMBS developed here for bonding analyses will be exemplified in the subsequent paper by applications to cerium monoxide and cerium dioxide.\textsuperscript{23}

2. Methods

2.1 Saturated Gaussian primitive basis sets

Relativistic AAMBS orbitals for the elements Li - Xe were previously computed using the saturated well-tempered basis sets (WTBS) of Huzinaga et al. that used a shared set of well-tempered exponents for all orbital types.\textsuperscript{24,25} The present development of AAMBS orbitals for Cs – Rn also employs well-tempered basis sets, but with new exponents optimized including the influence of scalar relativistic effects. The optimizations take account of both the ground state and important low-lying excited states of the neutral atoms. The well-tempered basis sets also were optimized with independent sets of parameters for each \( l \) value, i.e. independent \( \alpha, \beta, \gamma, \) and
\( \delta \) parameters (Equations 1 and 2) and ranges for the \( s, p, d, \) and \( f \) functions. MOLPRO\textsuperscript{26} was employed for the optimization of the WTBS parameters, and the third-order Douglas-Kroll-Hess\textsuperscript{27-31} method was used to account for scalar relativistic effects. Since a point charge nuclear model was employed, an approach was needed to avoid optimization to extremely large Gaussian exponents. This is a common problem encountered in the development of basis sets for the heavy elements that results in numerical instabilities when computing integrals due to the large range of exponents, and this is particularly problematic when developing saturated basis sets.\textsuperscript{32} While a common remedy is to use a finite nucleus model,\textsuperscript{32-34} another remedy is to impose other constraints on the magnitude of the exponents. In the present work the original well-tempered recursion formula used by Huzinaga et al.\textsuperscript{24,25,35} was recast so that the \( \alpha \) parameter corresponds to the most compact basis function rather than the most diffuse (Eq. 1 and 2). The \( \alpha \) parameter for the \( s \) and \( p \) sets was then fixed so that the radial expectation value for the basis functions with an exponent equal to \( \alpha \) corresponded to the nuclear radius.\textsuperscript{36}

\[
\xi_{N'=\Lambda+1} = \alpha \quad \quad (1)
\]

\[
\xi_{N'=\Lambda+2} = \frac{\xi_{N'=\Lambda+1}}{\beta \left( 1 + \gamma \left( 1 - \frac{\xi}{\Lambda} \right)^5 \right)} \quad \text{k = 2, ..., N} \quad \quad (2)
\]

The WTBS parameters were energy optimized with a gradient convergence criterion of \( 10^{-6} \). All degenerate atomic orbitals were kept symmetry equivalent, and spherical harmonic functions were employed for the basis set optimizations. Since the QUAO orbitals in molecules may often involve several free atom configurations, the WTBS sets were optimized for the electronic configurations corresponding to the ground state and low-lying excited states. For example, the WTBS parameters for iridium were optimized for the \([\text{Xe}] \ 6s^24f^{14}5d^7 \) and \([\text{Xe}] \ 6s^14f^{14}5d^8 \)
configurations for each of the $s$, $p$, $d$, and $f$ sets with an additional [Xe] $6s^14f^45d^76p^1$ configuration for the $p$ functions. The additional electronic configuration for the $p$ functions was necessary since the AAMBS orbitals span the full valence space and the WTBS parameters for the $p$ functions must allow for sufficiently diffuse functions to describe the $6p$ orbitals. Since saturated basis sets were desired, basis functions were added to each of the $s$, $p$, $d$, and $f$ sets and the WTBS parameters were re-optimized until the atomic energies converged to 1 $\mu$E$_h$ as a function of the number of Gaussian exponents for all electronic configurations. The optimized well-tempered parameters $\alpha$, $\beta$, $\gamma$, $\delta$ used to generate the exponents and the electronic configurations used for the various atoms in the optimization of the well-tempered parameters are shown in tables S1 – S8 of the Supporting Information.

2.2 Accurate Atomic Minimal Basis Set (AAMBS) orbitals

Full valence AAMBS orbitals have been developed for the 6$^{th}$ row elements cesium through radon, thus extending the availability of the AAMBS orbitals$^{15}$ to include all elements up to radon. The aforementioned saturated WTBS primitive sets were used in the computation of the AAMBS orbitals. Scalar relativistic effects were incorporated into the AAMBS orbitals for cesium and heavier elements using the infinite order two-component method (IOTC)$^{37-40}$ implemented in the GAMESS$^{41-43}$ quantum chemistry software package. The IOTC transformation is effectively the Douglas-Kroll-Hess procedure carried out to infinite order and is exact for one electron Dirac problems.$^{31,44}$ The AAMBS orbitals for the elements in the $p$-block were computed using open- or closed-shell self-consistent field (SCF) calculations for the neutral atoms. Only the ground state was computed for the $p$-block elements with radial
degeneracy enforced for the $p$ orbitals resulting in a spherically symmetric density. Thus, the $^2P$, $^3P$, $^4S$, $^3P$, $^2P$, and $^1S$ states were computed for Tl, Pb, Bi, Po, At, and Rn, respectively.

The AAMBS orbitals for cesium and barium were computed for the full valence space ($6s$, $5d$, $6p$). The $4f$ orbitals were excluded since the lowest state that has the $4f$ orbitals occupied in cesium is the $^2F$ state that lies 24472 cm$^{-1}$ above the ground state, and the lowest state that has the $4f$ orbitals occupied in barium is the $^3F$ state that lies 34603 cm$^{-1}$ above the ground state. In fact, electronic states arising from the occupation of the $6d$, $7s$, $7p$, and $8s$ orbitals have lower energies than do those obtained by occupying the $4f$ subshell, e.g. for cerium the $^2S$, $^2P$, $^2D$, and $^2S$ states corresponding to the [Xe] $7s^1$, [Xe] $7p^1$, [Xe] $6d^1$, and [Xe] $8s^1$ configurations, respectively, are at lower energies than the $^2F$ state that corresponds to a [Xe] $4f^1$ configuration. A state-averaged density was computed that was averaged over the $^2S$, $^2P$, and $^2D$ states for cesium and the $^1S$, $^3P$, and $^3D$ states for barium. The state averaging was performed so that each Russell-Saunders term was weighted equally while maintaining the 3-fold and 5-fold radial degeneracies of the $p$ and $d$ orbitals, respectively. This was achieved using the full configuration interaction (CI) determinant-based MCSCF program in GAMESS. The orbital occupancy was enforced using the occupation restricted multiple active space (ORMAS) method in GAMESS.

The AAMBS orbitals for the transition metals and lanthanides were computed in a similar manner to the $s$-block. However, the optimization of the AAMBS orbitals for the transition metals and lanthanides often involved a two-step optimization procedure analogous to the procedure that previously was employed for the $3d$ and $4d$ transition metals. In the first step the orbitals occupied in the ground state were optimized, e.g. the [Xe] core, $6s$, $4f$, and $5d$ depending on the ground state electronic configuration. For example, the initial optimization of
the occupied orbitals for neodymium included the [Xe] core and the 6s and 4f orbitals since the ground state configuration is [Xe] 6s^24f^4, whereas the initial optimization of the occupied orbitals for platinum included the [Xe] core and the 6s, 4f, and 5d orbitals since the ground state configuration is [Xe] 6s^14f^45d^9. All possible determinants were allowed to mix when computing the state-averaged density, though only the selected L-S terms were included in the density resulting in multireference character being incorporated into the state-averaged density. For example, the [Xe] 6s^14f^45d^9 and [Xe] 6s^24f^45d^8 configurations of platinum were computed in the first optimization step. These two electron configurations give rise to 3D and 1D terms and 3F, 3P, 1G, and 1D terms, respectively. After consideration of experimental energies of these terms, only the 3D and 1D terms from the [Xe] 6s^14f^45d^9 configuration and the 3F term from the [Xe] 6s^24f^45d^8 configuration were included in the state-averaged density. The SA-MCSCF program based on ORMAS occupancies [Xe] 6s^14f^45d^9 and [Xe] 6s^24f^45d^8 involves enough determinants to include all terms, but only the desired low lying terms were given weight during the AAMBS orbital optimization.

The second step in the two-step optimization of the AAMBS orbitals involves optimization of the 6p orbitals for the transition metals, and often the 5d and 6p orbitals for the lanthanides that are not occupied in the ground state. A subsequent ORMAS SA-MCSCF calculation is performed whereby an electron is promoted to the 6p or 5d subshell from the 6s orbital. After consideration of the experimental energies to select the appropriate new terms, the previously optimized occupied orbitals are frozen and only the 6p or 5d orbitals are optimized.

Table 1 summarizes the L-S terms used in the optimization of the AAMBS orbitals for the transition metals. The ground state and low-lying excited state terms are given for both the
first and second step of the optimization process. \( \Delta E_1 \) corresponds to the maximum energy difference between the ground state and the highest energy excited state included in the state averaged calculation of the occupied orbitals, and \( \Delta E_2 \) corresponds to the maximum energy difference between the ground state and the highest energy excited state term included in the optimization of the valence orbitals that are unoccupied in the ground state. The energy difference between the ground and highest excited state used in the initial optimization of the density is below 40 kcal mol\(^{-1}\) for the transition metals with the exception of iridium and gold that have energy ranges of 57.8 kcal mol\(^{-1}\) and 61.2 kcal mol\(^{-1}\), respectively. Promotion of an electron to the 6\(p\) orbitals is a high-energy process for the transition metals with energy ranges in excess of 67.5 kcal mol\(^{-1}\) and as high as 125.8 kcal mol\(^{-1}\) for mercury.

The L-S terms used in the computation of the AAMBS orbitals for the lanthanides are shown in Table 2 along with the maximum energy ranges of the excited state terms used in the first step (\( \Delta E_1 \)) and second step (\( \Delta E_2 \)) of the orbital optimization procedure. The unsaturated nature of the lanthanides frequently resulted in a large number of L-S terms included in the ORMAS SA-MCSCF calculations. This is particularly pronounced for some of the early lanthanides. In the case of lanthanum, i.e. the most unsaturated of the lanthanides, 15 L-S terms were included in the state averaged density with an energy range of 43.4 kcal mol\(^{-1}\). A single step optimization was performed for lanthanum, promethium, europium, and gadolinium. For these, occupation of the 5\(d\) and 6\(p\) orbitals occurs at relatively low energies with a maximum energy range between the ground state and the highest energy state included in the ORMAS SA-MCSCF calculations occurring for gadolinium with an energy range of only 51.5 kcal mol\(^{-1}\).

The AAMBS orbitals for the remaining lanthanides were optimized with the two-step process. For the two-step process, the initial orbital optimization was performed for the ground
state and low-lying excited states that share the same symmetry in the \( C_i \) point group. \( C_i \) symmetry was enforced as this is the highest order point group for which each orbital type has the same symmetry, e.g. all \( f \) orbitals have \( A_u \) symmetry, all \( d \) orbitals have \( A_g \) symmetry, etc. When the two-step optimization process was performed, the largest energy difference between the ground and excited states of the same symmetry occurred for samarium with an energy range of 42.6 kcal mol\(^{-1}\). The occupied orbitals from this initial optimization were then frozen and the \( 5d \) and \( 6p \) orbitals were optimized to recover AAMBS orbitals for the full valence space. The energy range between the ground state and the highest energy excited state used in the second optimization step ranged from 38.6 kcal mol\(^{-1}\) for the \( 5G \) state of cerium (\([Xe] \, 6s^1 \, 4f^1 \, 5d^1 \, 6p^1 \)) to 74.5 kcal mol\(^{-1}\) for the \( 8G \) state of terbium (\([Xe] \, 6s^1 \, 4f^9 \, 6p^1 \)).

3. Conclusions

Relativistic AAMBS orbitals have been developed for the 6\(^{th}\) row elements cesium to radon, extending the availability of these orbital sets for use both in constructing valence virtual orbitals and in the construction of oriented QUAOs. Thus, the intrinsic quasi-atomic bonding analysis, which is implemented in GAMESS, can be used to examine bonding in \( 6s \), \( 4f \) (lanthanide), \( 5d \), and \( 6p \) elements. In keeping with the previously developed formalism,\(^{15}\) these new additions to the AAMBS sets span the full valence spaces, i.e. the AAMBS for the 6\(^{th}\) row elements consists of \( 4f \), \( 5d \), \( 6s \), and \( 6p \) valence orbitals (along with the \([Xe]\) core, of course), except for Cs and Ba where no \( 4f \) is present in the AAMBS. In the course of this work, support for relativistic integrals over \( h \) and \( i \) functions also was implemented to enable the use of the full correlation consistent,\(^{32,34,49}\) Sapporo,\(^{50,51}\) and all other basis sets with high angular momentum in the study of heavy element chemistry. An illustration of the effectiveness of the AAMBS to the
understanding of 4f participation of bonding by cesium is provided in the following paper. Contraction coefficients to form the AAMBS for all elements Li-Rn by the procedures described both here and in reference 15 are freely available for download.²¹

Supporting Information

The Supporting information is available free of charge on the ACS Publications website. Well-tempered basis set (WTBS) parameters; electronic configurations used in the optimization of the WTBS parameters; ground state energies obtained with the saturated well-tempered basis sets

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Dr. Ivanic for his assistance implementing the relativistic integrals over h and i functions.
References


Table 1. Summary of the terms and valence configurations used in the state-averaged multiconfigurational self-consistent field (SA-MCSCF) calculations to optimize orbitals occupied in the ground and low-lying excited states for the 5d transition metals. $\Delta E_1$ corresponds to the experimental energy separation in kcal mol$^{-1}$ between the lowest $J$ level of the ground state L-S term and the highest energy excited L-S term used in the state averaged calculations. The italicized columns correspond to excited states used with a two-step procedure to optimize the 5d and 6p orbitals, and $\Delta E_2$ corresponds to the experimental energy separation in kcal mol$^{-1}$ between the lowest $J$ levels of the ground state L-S term and the highest energy excited L-S term used in the two-step procedure.

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<th>Atom</th>
<th>Ground State</th>
<th>Excited State(s)</th>
<th>$\Delta E_1$</th>
<th>Excited State(s)</th>
<th>$\Delta E_2$</th>
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<tr>
<td>Hf</td>
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<td>$^3$P 6s$^2$ 4f$^{14}$ 5d$^5$</td>
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<td>$^3$G 6s$^2$ 4f$^{14}$ 5d$^5$ 6p$^1$</td>
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<td>$^5$P 6s$^2$ 4f$^{14}$ 5d$^3$</td>
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<td>$^3$P 6s$^2$ 4f$^{14}$ 5d$^{10}$ 6p$^1$</td>
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Table 2. Summary of the terms and valence configurations used in the state-averaged multiconfigurational self-consistent field (SA-MCSCF) calculations to optimize orbitals occupied in the ground and low-lying excited states for the lanthanides. ΔE₁ corresponds to the experimental energy separation in kcal mol\(^{-1}\) between the lowest \(J\) level of the ground state L-S term and the highest energy excited L-S term used in the state averaged calculations.\(^{45}\) The italicized columns correspond to excited states used with a two-step procedure to optimize the 5d and 6p orbitals, and ΔE₂ corresponds to the experimental energy separation in kcal mol\(^{-1}\) between the lowest \(J\) levels of the ground state L-S term and the highest energy excited L-S term used in the two-step procedure.

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<th>Atom</th>
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<th>Excited State(s)</th>
<th>(\Delta E_2^a)</th>
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<td>(^4)F 6s(^1) 5d(^2), (^4)P 6s(^1) 5d(^2), (^4)F 6s(^1) 5d(^1) 6p(^1), (^2)F 6s(^1) 5d(^2), (^4)D 6s(^1) 5d(^1) 6p(^1), (^2)D 6s(^1) 5d(^2), (^2)G 6s(^1) 5d(^2), (^2)D 6s(^1) 5d(^1) 6p(^1), (^4)P 6s(^1) 5d(^1) 6p(^1), (^2)P 6s(^1) 5d(^1) 6p(^1), (^2)P 6s(^1) 5d(^2), (^2)F 6s(^1) 5d(^1) 6p(^1), (^2)P 6s(^1) 5d(^2), (^2)F 6s(^2) 4f(^1)</td>
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</tr>
<tr>
<td>Pm</td>
<td>(^6)H 6s(^2) 4f(^5)</td>
<td>(^6)F 6s(^2) 4f(^5), (^8)K 6s(^1) 4f(^5) 5d(^1), (^8)l 6s(^1) 4f(^5) 6p(^1), (^7)G 6s(^1) 4f(^5) 6p(^1)</td>
<td>21.1(^a)</td>
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<tr>
<td></td>
<td>7F 6s² 4f⁶</td>
<td>²H 6s⁴ 4f⁵ 5d¹</td>
<td>³G 6s⁴ 4f⁶ 6p¹</td>
<td>54.3</td>
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<tr>
<td>Sm</td>
<td>⁷S 6s² 4f⁷</td>
<td>¹⁰D 6s¹ 4f⁶ 5d¹</td>
<td>⁹F 6s¹ 4f⁶ 6p¹</td>
<td>47.5</td>
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<tr>
<td>Eu</td>
<td>⁸G 6s² 4f⁸ 5d¹</td>
<td>¹¹F 6s¹ 4f⁶ 5d¹</td>
<td>¹⁰P 6s¹ 4f⁶ 5d¹</td>
<td>51.5</td>
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<tr>
<td>Gd</td>
<td>⁹D 6s² 4f⁵ 5d¹</td>
<td>¹²D 6s¹ 4f⁶ 5d¹</td>
<td>¹¹P 6s¹ 4f⁶ 5d¹</td>
<td>29.5</td>
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</tr>
<tr>
<td>Tb</td>
<td>⁸G 6s² 4f⁵ 5d¹</td>
<td>¹³D 6s¹ 4f⁶ 5d¹</td>
<td>¹²P 6s¹ 4f⁶ 5d¹</td>
<td>74.5</td>
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</tr>
<tr>
<td>Dy</td>
<td>⁵I 6s² 4f⁰</td>
<td>²¹I 6s² 4f⁰ 6p¹</td>
<td>²⁷I 6s² 4f⁰ 5d¹</td>
<td>⁶¹.⁴⁹</td>
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</tr>
<tr>
<td>Ho</td>
<td>⁴I 6s² 4f¹¹</td>
<td>²⁷H 6s² 4f⁰ 6p¹</td>
<td>²⁷K 6s² 4f⁰ 5d¹</td>
<td>⁵⁷.⁸⁹</td>
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<tr>
<td>Er</td>
<td>³H 6s² 4f¹²</td>
<td>³F 6s² 4f¹²</td>
<td>²⁷G 6s² 4f⁰ 5d¹</td>
<td>⁵⁷.⁵⁹</td>
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<tr>
<td>Tm</td>
<td>²F 6s² 4f¹³</td>
<td>⁴D 6s¹ 4f¹² 6p¹</td>
<td>⁴D 6s¹ 4f¹² 6p¹</td>
<td>⁶⁰.⁷⁹</td>
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<tr>
<td>Yb</td>
<td>¹S 6s² 4f¹⁴</td>
<td>²⁷P 6s¹ 4f¹² 6p¹</td>
<td>²⁷P 6s¹ 4f¹² 6p¹</td>
<td>⁵⁶.³³</td>
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</table>
The energy difference corresponds to the computed energy difference rather than an experimental energy difference. This is due to the lack of a definite assignment of L-S terms to the experimental levels.

b The $^8G$ state was taken as the ground state rather than the $^6H$ state. This is because the lowest $J$ levels are within 1 kcal mol$^{-1}$ of each other and using the $^8G$ state allows the 5d orbitals to be occupied in the first step of the two-step optimization.
\[ \xi_N = \alpha \]

\[ \xi_{N-k+1} = \frac{\xi_{N-k+2}}{\beta (1 + \gamma (1 - \frac{k}{N}))} \quad k = 2, \ldots, N \]