

**Binding energies, hyperfine structure,
and magnetic dipole decay rates for $\text{Os}^- 5d^7 6s^2 \ ^4\text{F}$
levels**

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Relativistic Configuration Interaction (RCI) calculations predict that the $5d^7 6s^2 \ J = 9/2, 7/2, 5/2$ and $3/2 \ ^4\text{F}$ levels of Os^- are all bound with binding energies (BE) 1.048, 0.508, 0.292, 0.211 eV, respectively. To aid future experimental work, hyperfine structure constants for all levels and magnetic dipole decay rates have also been calculated.

I. INTRODUCTION AND METHODOLOGY

In this work, we continue our studies of transition metal (TM) electron affinities (EA) done in collaboration with the McMaster experimental group [1]. Except for Tc^- and Re^- , the least studied [2] TM species is Os^- , for which there only exists a semi-empirical Os EA. Interpolation predicts [3] a $d^7s^2\ ^4F$ bound state with a binding energy (BE) of ~ 1.1 eV. *Ab initio* treatments of such high Z species require the simultaneous inclusion of correlation and relativistic effects. For us, the method of choice is that of Relativistic Configuration Interaction (RCI).

Although Os^- is homologous to Ru^- , which we have dealt with in an earlier study [4], the ground states of the atoms are not identical [5], having configuration d^7s for Ru and d^6s^2 for Os. For Os, this means we are attaching a d electron to the ground state to form the negative ion. For the RCI method as we currently employ it, attachments of d electrons are more difficult to treat, as they involve more of the core than do s or p attachments. To avoid dealing with this, we use an excited d^7s level [5] in Os I, and make an s attachment to it. This attachment energy is then “corrected” using the experimental energy difference [5] in Os I, which automatically includes the difficult-to-treat core effects associated with d attachment. This approach has been used before by us [6], and even earlier by Vosko *et al* [7] and ourselves [8]. For both Ru^- [4] and Os^- , quadruple excitations (second order effects) have a significant impact on the BE, increasing it ~ 100 meV.

We begin with numerical solutions [9] of the Dirac-Fock equations, based on the Dirac-Coulomb Hamiltonian for the dominant configurations, here $5d^76s^2$ for Os^- and $5d^76s$ for Os. Construction of the RCI matrix, based on a first order form, begins by making single and double excitations from the Dirac-Fock (DF) configuration valence subshells ($5d$, $6s$ for Os/ Os^-) into existing open subshells, or new ones, called virtuals. The radial parts of the virtual functions are represented by relativistic screened hydrogenic (RSH) functions whose charge (Z^*) is determined during the RCI variational process [10]. Generally, two RSH functions per l are adequate to achieve $\sim 95\%$ of the correlation energy, and for most

purposes $l \leq 4$ is appropriate (see Table I of Ref. [4]).

How much of the core is to be opened depends on the application and resources available. More of the core should be needed if one calculates the BE of X^- relative to X (e.g., Os^- $J = 9/2$ relative to Os $J = 5$), rather than relative to another X^- state (e.g., Os^- $J = 7/2$ relative to Os^- $J = 9/2$). Here we have opened $5p$ for Os and $J = 9/2$ Os^- , and have no opened core for the other Os^- states. To justify this, for the $J = 7/2$ Os^- level, we can cite the agreement between experiment and theory for the Ru^- $J = 7/2$ BE [4], using the same expansions we use for Os^- .

As we add configurations to the RCI wave function, we find that some of the most significant valence correlations, such as $6s^2 \rightarrow 6p^2$ and $6s \rightarrow s$, decline. A reason for this [11] is that these correlation configurations are not being as carefully correlated as the DF configuration, which is consequently being “pulled away” from them. This decreases their contribution to the correlation energy. This can be rectified by including the equivalent correlation configurations for the important correlation configurations cited above. As an illustration for Os^- , the decline of the $5d^7 6p^2$ contribution as $5d6s$ excitations (to DF) are included can be compensated for by including $5d6p$ excitations from it. These are triple excitations with respect to DF. Thus, they are to be associated with a second order form for the wave function.

But for Os^- and Ru^- [4] there are additional important second order effects associated with the excitations from $5d^2 6s^2$. The largest of these can be viewed as being formed from the important (see Table I of Ref. [4]) $5d6s$ pair excitations, viz. $5d6s \rightarrow pf + p^2 + sd$. All the second order effects included are present in Os^- , but not in Os . For our Os^- calculations, like for Ru^- [4], we include no $5d^2$ pair correlation; we argue that the $5d^7$ electrons are essentially coupled to a 4F in both Os and Os^- , so that this pair correlation should nearly cancel. This is expected to be even more valid when comparing two negative ion states.

For Os/Os^- , many of the correlation configurations have hundreds, if not more, of eigenvectors; if these were all kept, a rather large RCI matrix (perhaps 50 000 to 100 000) would be generated. From our perspective, this entails a rather large computational expense, but

can also make it more difficult to analyze, interpret, and use the resulting wave function.

There is a method, called REDUCE, by which the size of the matrix can be drastically decreased [4,12,13], with apparently little loss of energy (~ 10 – 20 meV). Corresponding errors in hyperfine structure constants are likely to be moderate, unless there is a nearby (1–2000 cm^{-1} , see Ref. [14]) $5d^86s$ level which strongly interacts with a $5d^76s^2$ level. Since correlation effects are usually quite moderate (1% here) for $M1$ rates (an exception is for Sn^- , see Ref. [11]), errors due to REDUCE are likely to be quite modest. In any case, there seems to be no algorithm currently available capable of reducing errors below 10–20 meV for energy differences of such complicated states.

In the first step of REDUCE, the origins (or reference functions) of each “complicated” configuration are determined. For configurations in the first order wave function, one origin is the DF configuration, for Os^- another might be the $5d^76p^2$ configuration. For second order configurations, origins are part of the first order function. In all cases, the origins are those configurations interacting most strongly with the configuration we wish to REDUCE. We then rotate its eigenvectors to maximize the number of zero interactions we have with all origin eigenvectors. These zero interacting rotated eigenvectors can then be discarded. Reductions in the number of eigenvectors by factors of 10 to 1000 can be achieved—the greater reductions actually occur for more complicated configurations (desirable), but less reduction occurs for second order origins than for first order ones.

Once the RCI wave functions are generated, both hyperfine structure (HFS) constants (dipole and quadrupole) and magnetic dipole ($M1$) decay rates are obtained. Expressions for HFS matrix elements have been given elsewhere [13] and are based on earlier work of Lindgren and Rosen [15].

Expressions for $M1$ transition rates have been given in Ref. [11]; they are based on the work of Grant [16]. It should be noted that since the RCI wave functions are obtained independently of one another, their basis sets are not orthonormal. In calculating the $M1$ decay rates, nonorthonormality effects are fully accounted for [17] following the work of King *et al* [18].

The Breit contribution has been treated only at the average [9] energy DF level. For the $\text{Os}^- J = 9/2$ BE, non-average magnetic effects are only 0.05 meV. Breit contributions to Os^- BEs are small, between 1 and 15 meV, so that a more thorough treatment is unnecessary.

II. RESULTS

For Os/Os⁻, RCI calculations begin by making single and pair excitations from the outermost *s* electrons; these pair excitations are present only in the negative ion. Energy contributions are determined by use of second order perturbation theory [14]. The most important of these valence correlations in Os⁻ $J = 9/2$ are $s^2 \rightarrow p^2$, $s \rightarrow s$, and $s^2 \rightarrow s^2$. We carefully monitor these contributions as we excite (open) from the core, and when we observe significant changes, introduce triple and quadruple excitations, which tend to partially compensate for these losses. Valence excitations seem (see Table I of Ref. [4]) to be adequately described by $l = 0$ to 4 and by one radial function per l , except for the p symmetry, which uses two.

The next step is to include the pair excitations $ds \rightarrow$ and single excitations from the d shell. These are the major contributors to the BE (the DF contributions are negative in fact), with the $ds \rightarrow sd + p^2 + pf$ being the largest. Introduction of these excitations decreases the valence contributions, particularly $s^2 \rightarrow p^2$, by as much as several tens of meV. This is partly because we have treated d^7s^2 and d^7p^2 unequally; we have included $ds \rightarrow$ in the former, but not dp excitations in the latter. When these are introduced (and they are triple excitations with respect to d^7s^2 ; the specific triples included are listed in Table I of Ref. [4] by symmetry type), about 1/3 of the energy lost is restored. Coefficients of these triples can be as large as 0.01 in magnitude. Both ds and dp excitations generated manifolds that are so complicated (number of parents, determinants), that the REDUCE methodology [12,13] is used to introduce them. The important role (~ 100 meV here) played by the quadruple excitations such as $5d^26s^2 \rightarrow vp^2vf^2$ can be most clearly seen in Table I of our Ru⁻ work [4].

We note that no d^2 excitations are included here. We exclude them, because we believe their large contributions to the total energy make almost no contribution to the Os EA. Furthermore, if they were introduced they would have to be treated in a very balanced way (equivalent basis sets) for atom and ion, and they would have a significant impact on

the valence correlations, necessitating the need for the introduction of further (partially) compensating triple and quadruple excitations.

The next computation step is to include ps excitations. These contribute 76 meV to the Os EA. Opening this shell also impacts the valence excitations, which is partially compensated for by the inclusion of $5p6p$ excitations from $5d^76p^2$. In the process of opening this subshell, it was noted that there was a decrease in the important $5d6s \rightarrow pf$ contributions (there is a strong $d^2 \rightarrow pf$ interaction between the two, as expected [19]). However, this change (total energy) had almost zero impact on the Os EA.

To simplify calculations for the $J = 7/2, 5/2, 3/2$ Os⁻ states, we argue as in Sn⁻ [11] that there is much correlation in common with the $J = 9/2$ state. There is a “first order” theoretical basis for this [20], which applies if (among other conditions) the radial functions for the states do not vary much, and at least one of the two subshells being excited is initially closed. Greater cancellation also ensues because all ion states are associated (mainly) with the same $d^7 4F$ configuration. In this case, we specifically have not opened the p subshell for the $J = 7/2, 5/2, 3/2$ states, locating them instead with respect to the $J = 9/2$ state (using a $J = 9/2$ wave function with the $5p$ subshell closed).

The $J = 5$ and large $J = 9/2$ calculations have 3902 and 3954 parents respectively; whereas the smaller $J = 9/2, 7/2, 5/2,$ and $3/2$ calculations have 1730, 1972, 2075, and 1737 vectors respectively. Matrix sizes were kept moderate by employing REDUCE; for example, for the $5d^5vp^2vf^2$ configuration for $J = 9/2$, only 33 rotated vectors out of the original 4598 vectors need to be kept (a factor of 139 reduction).

The binding energies for all states are reported in Table I; it can be seen that the ion is unbound at the DF level. Table II contains results for magnetic dipole (A) and electric quadrupole/quadrupole moment (B/Q) constants. Nuclear constants are taken from Fuller and Cohen [21] and Raghavan [22]. For Os I, very accurate experimental results are available [23] for A and B/Q . Our results are in good agreement with these, though the accuracy should be improved by including core excitations such as $5s \rightarrow s+d$ and $5p \rightarrow p+f$, as we do in more thorough HFS studies [14]. The largest correlation contributions to the calculated

A are the $6s \rightarrow s$ and $5d \rightarrow d$ excitations. The variation in the correlation correction to A for the $J = 3/2$, $5/2$, and $7/2$ states comes mainly from the changing magnitude and sign of the $6s \rightarrow s$ excitation. As the $J = 3/2$, $5/2$, and $7/2$ states have smaller RCI expansions, their HFS constants are likely less accurate than those for $J = 9/2$ and $J = 5$.

Table II also contains RCI magnetic dipole decay rates for the Os^- states; these differ little (1%) from the DF values. Both the HFS and $M1$ results may be useful [1] in experimental studies of these ions. We have also calculated electric quadrupole ($E2$) decay rates for the Os^- states; these were generally several orders of magnitude smaller than the $M1$ rates, so they are not included in Table II.

If the Ru^- results are a guide, the RCI BE of Os^- $J = 9/2$ may be in error ~ 30 meV and the $J = 7/2 - J = 9/2$ splitting ~ 10 meV. It seems likely that the positions of the $J = 3/2$ and $5/2$ levels relative to $J = 9/2$ may also be rather accurately determined.

TABLE I. Binding energies (BE) of $5d^7 6s^2$ “ $4F$ ” states of Os^- .

State	BE (eV)		
	DF	corr	Total ^a
$\text{Os}^- 5d^7 6s^2$			
$J = 9/2$	-0.0979	1.7770	1.048 ^b 1.1(2) ^c
$J = 7/2$	-0.6636	1.0059	0.508 ^b
$J = 5/2$	-0.9159	1.0428	0.292 ^b
$J = 3/2$	-1.0757	1.1238	0.211 ^b

^aDF + corr. + magnetic Breit.

^bDF + corr. + magnetic Breit - $\Delta E(5d^7 6s J = 5 - 5d^6 6s^2 J = 4)$. The last quantity is experimental, from Moore [5].

^cSemi-empirical (extrapolated) value from Feigerle *et al* [3].

TABLE II. Hyperfine structure constants and magnetic dipole decay rates for $\text{Os}^- 5d^7 6s^2 \text{ } ^4\text{F}$ and $\text{Os} 5d^7 6s \text{ } ^5\text{F}$ $J = 5$ states.

State	HFS ^a						$M1 \text{ (s}^{-1}\text{)}^b$
	A (MHz)			B/Q (MHz/b)			
	DF	RCI	Expt	DF	RCI	Expt	
$\text{Os}^- 5d^7 6s^2$							
$J = 9/2$	214	386		494	448		
$J = 7/2$	240	268		467	434		2.17
$J = 5/2$	277	275		434	403		0.173
$J = 3/2$	382	308		7.3	16.6		0.00634
$\text{Os} 5d^7 6s$							
$J = 5$	-219	-224	-229 ^d	342	318	348 ^d	

^aFor Os/Os^- $\mu = 0.6566$, $I = 3/2$, $Q = 0.85$; μ and I from Fuller and Cohen [21] and Q from Raghavan [22].

^bIn accordance with magnetic dipole selection rules ($\Delta J = 0, \pm 1$), decay from the J level occurs only to the $J + 1$ level.

^cDF values differ by $\sim 1\%$.

^dExperimental values [23] are given to more significant figures.

III. ACKNOWLEDGMENT

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