Brief Reports

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Bound states in Mn^-

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We have identified the four lowest bound states of Mn^-: $3d^54s4p^2\,^9P_j$ (E_A=0.586,0.597,0.607 eV for J=5,4,3, respectively) and $3d^54p^3\,^9S^\circ_4$ (E_A=0.470 eV). The electric dipole oscillator strength connecting ^9P and $^9S^\circ$ is 0.343 (length) and 0.299 (velocity). Our energetic results include both relativistic and many-body effects. We find that a relativistic zeroth-order function involving open d and p electrons may characteristically involve over 100 configurations.

I. INTRODUCTION

This work is the third[1,2] reporting on studies of first-row transition-metal negative ions. As discussed previously,[1,2] these species can involve substantial relativistic effects, and the presence of 3d-subshell electrons places extra demands on one- and many-electron basis sets used to correlate the system. The states of Mn^- studied here, $3d^54s4p^2\,^9P$ and $3d^54p^3\,^9S^\circ$, were uncovered by applying some general rules of thumb[1] for possible bound-state (i.e., here, states which do not nonrelativistically autoionize) candidates, and then performing restricted Hartree-Fock (RHF) calculations[3] to identify the most favorable cases. Mn^- was a particularly attractive choice for further exploration, in our opinion, because of the following: (1) there are no known[4,5] bound states and (2) it involves a maximum number of open d-shell electrons (holes) in comparison to our earlier cases[1,2] (Sc, Zn, Cu) which had at most one open d-subshell electron (hole), and is thus a more complicated problem.

II. MANY-ELECTRON EFFECTS

Our previous work[1,2] suggests that when the diffuse and relatively isolated 4p electron is added to the threshold (here, "actual" and "natural" thresholds[1] coincide), contributions to the differential correlation arise chiefly from N-shell correlation and $3d-N$-shell correlation, and that we can confine our attention to pair correlation—providing we are satisfied with accuracies on the order of 0.1 eV.

In Table I we display the RHF and many-electron contributions to the electron affinity (EA). We see that both

TABLE I. Energy contributions to states of Mn^- and their thresholds.

State	RHF energy[a]	N-shell correlation[b]	$3d-N$-shell correlation[b]	Relativistic contribution[c]	LS purity
$3d^54s4p^2\,^9P_5$	−1149.833 545	−13.00	−21.99		99.92
$3d^54s4p\,^8P^\circ_{9/2}$ (threshold)	−1149.827 060	−5.47	−21.09		
Difference (eV)	0.176	0.204	0.025	0.065[d]	99.98
		E_A=0.470 eV			
$3d^54p^3\,^9S^\circ_4$	−1149.668 020	−17.47	−20.54		95.9
$3d^54p^2\,^9P_{9/2}$ (threshold)	−1149.659 626	−6.61	−18.75		97.1
Difference (eV)	0.228	0.295	0.049	+0.014	
		E_A=0.586 eV			

[a]In hartrees.
[b]In 10^{-3} hartrees.
[c]In eV.
[d]The ^9P_J energies [relative to J=5: −0.011 eV (J=4) and −0.021 eV (J=3)].

EA's are both fairly large, and are comprised of nearly equal RHF and N-shell correlation contributions. On the other hand, $3d4s+3d4p$ pair correlation is about 10% of the former contributions. This correlation involves configurations with too many parents and determinants to be conveniently treated with the older techniques.[6] Instead, we use REDUCE (Refs. 1 and 2) which rotates the original space so as to minimize the number of parents which have a nonzero interaction with the zeroth-order function. The other parents are then discarded. When the zeroth-order function is chosen to be the RHF solution, there are only a few (≤ 6) survivors and a minimal[2] loss of accuracy.

III. RELATIVISTIC EFFECTS

We will treat relativistic effects by solving the Dirac-Fock (DF) problem. Here,[2] the Hamiltonian used during the self-consistent field (SCF) stage[7] consists of the sum of one-electron Dirac operators and the Coulomb interaction between electrons. All relativistic configurations that reduce to the nonrelativistic one as $c \rightarrow \infty$ are included, so we have a multiconfigurational DF problem. There were as many as 210 of these for the states considered here, necessitating a redimensioning of the Desclaux program[7] as well as a change in its packing schemes (arrays ICJC and IJLMK of subroutine LIRFGR). We expect that many problems will be of similar size when open d-shell and open p-shell electrons (holes) are present.

To illustrate this configurational "explosion" consider $3d^5 4p^3\,{}^9S^\circ_4$. Relativistically, we have

$$3d^r_{3/2}\,3d^{5-r}_{5/2}\,4p^s_{1/2}\,4p^{3-s}_{3/2}$$

with $r \leq 4$ and $s \leq 2$. Any choice producing a total $J=4$ is acceptable—subject to Pauli exclusion restriction associated[8] with multiple occupancy of subshells (nlj). In the present case, there are 120 possibilities. One many additionally impose various couplings, providing a complete orthonormal basis is maintained. We have found it best to impose the subcouplings with an eye toward the nonrelativistic limit. Here, we couple the subgroup of the five d electrons to a specific J' and the three p electrons to their own J''. Such coupling is imposed by program RELCOR developed by one of us.[9] In the nonrelativistic limit, $J'=\frac{5}{2}$ and $J''=\frac{3}{2}$ (stemming from the d^5 electrons being nonrelativistically coupled to a ${}^6S$ and the p^3 to a ${}^4S$). If the relativistic result were to be nearly LS then weights of configurations corresponding to other J',J'' values would be expected to be small.

The correct (i.e., level-dependent) electrostatic structure must be input to the DF program. This is done by RELCOR.[9] For the number of configurations involved here, there are as many as 37 000 extra integrals (our coupling choice also serves to hold this number down) which also required increasing the dimensions of the DF program.[7] To reduce computing costs, it is wisest to group all two-electron electrostatic radial integrals having the same arguments (only the parental weights and angular factors differing) together. Two-electron relativistic effects are calculated by applying first-order perturbation theory to the Breit operator using the DF solution.

Once again, due to the diffuseness and relative isolation of the $4p$ electron, the "nonaverage" radial Breit integrals are small (for cases where such effects are significant, see Cheng, Desclaux, and Kim[10]); hence, our results only include the average Breit contributions.

Both Mn^- states required "better" input than previously needed.[1,2] For Mn^- $3d^5 4p^3\,{}^9S^\circ_4$, screened hydrogenic input, with screening constants obtained from RHF results[3] we produced, was used. However, it was necessary to correct the DF program by resetting the effective Z to the true nuclear charge (in subroutine SCFDAT) *prior* to the first iteration (without this correction, the first iteration is performed with the last effective charge used for the screened hydrogenic estimates).

But, use of screened hydrogenic estimates was ineffectual for Mn^- $3d^5 4s 4p^2\,{}^9P_J$. Instead, as in the nonrelativistic case, we did isoelectronic series calculations, starting at $Z=25.5$, using the output for $Z=25.2$ and this output for $Z=25.0$ (we had previously modified the DF code[7] to handle noninteger Z's).

The relativistic contributions to the EA's are shown in Table I; as is usual for these cases when a $4p$ electron is added, the contribution is only a few hundredths of an eV. Also shown in Table I is the fine structure for Mn^- $3d^5 4s 4p^2\,{}^9P$ obtained from zeroth-order DF calculations; the splitting is small (0.01 eV) and the $J=3$ state lowest. As the two threshold fine structures are already available,[11] they were not calculated here.

We produce LS eigenstates with RELCOR (Ref. 9) by neglecting[2] each spinor's minor radial component, and assuming that the major radial components are independent of j (a prescription also favored by Bessis, and Desclaux[12]) and diagonalizing the $\hat{L}^2$ and $\hat{S}^2$ matrices, treating all the relativistic configurations as one block. The DF wave function is then overlapped with the LS result; the square of the overlap being called the LS purity. For the states considered here, all purities are $\geq 96\%$ (see Table I).

One may inquire what the effect would be of deleting the non-LS configurations from the zeroth-order wave function. For $3d^5 4p^3\,{}^4S^\circ_4$ this reduces the number of configurations to 30 from 120, and also dramatically cuts down on the number of integrals. We have made this calculation for the ${}^9S$ and its threshold ($3d^5 4p^2\,{}^8P$) and find the EA changes by 0.15 eV to be essentially entirely due to changes in the ${}^9S$. This change is too large to permit advocating deletion of the "non-LS" configurations; moreover, they may play a significant role for properties other than electron affinities (and certainly can be expected to play a key role in the determination of lifetimes). It should also be remembered that such effects are only presently included, at best, in the zeroth-order function.

Finally, using the nonrelativistic N-shell correlation function, and including the effects of nonorthonormali-

ty[13] the $^9P \rightarrow {}^9S^\circ$ oscillator strength was found to be 0.343 (length) and 0.299 (velocity). This may aid in the optical detection of this species, in much the same manner as was done[14,15] for Li^-.

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