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# Possibility of formation of rare-earth negative ions by attachment of $f$ electrons to the atomic ground state

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Some recent experiments indicate that certain rare-earth negative ions exist. Some local-density calculations indicate that attachment of $f$ electrons is most favorable for Tm and Md. Here we investigate by means of relativistic configuration-interaction methods whether Tm$^-$ $4f^{14}$ and Md$^-$ $5f^{14}$ are bound. Our results strongly suggest that they are not, and that a different attachment process (perhaps that of a $p$ electron, as recently proposed by Vosko and Chevary [Bull. Am. Phys. Soc. **37**, 1089 (1992)]) must be contemplated.

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Not much is known about the electron affinity of the rare earths except for a few local-density calculations. Work by Bratsch on lanthanides [1] and by Bratsch and Lagowski on actinides [2] and more recent work of Guo and Whitehead [3] indicate that quite a few of these species may exhibit positive electron affinities when an $f$ electron is added. However the uncertainties in their electron-affinity values are sizable and are often as large as the electron affinities themselves. Recently however, Vosko and Chevary have predicted [4] a negative ion of lutetium by attaching a $p$ electron to the valence shell. Berkovits *et al.* have also reportedly observed negative ions of lanthanum and thorium in the laboratory [5] and Garwan *et al.* [6] have observed those of many of the lanthanides. However the electron configuration and electron affinity of none of these systems have been obtained experimentally. Tm$^-$ and Md$^-$ are predicted, by local-density theory [1,2] to be the most stable ones when an $f$ electron is added. For these reasons rare earths provide interesting systems for electron-affinity studies.

Tm$^-$ $[4f^{14}6s^2]$ and Md$^-$ $[5f^{14}7s^2]$ are among the simpler negative ions of rare earths due to their closed-shell nature. For these negative ions to exist their ground-state $(^1S_0)$ energies must lie below the ground-state $(^2F^o_{7/2})$ energies of the corresponding neutral atoms.

Unlike many other atomic properties, electron affinities are hard to determine with a small relative error. The negative ions are often so loosely bound that the effects usually regarded as small, especially electron correlation, may play a crucial role in binding them. Starting with the $3d$ transition series of the Periodic Table relativistic effects also affect the affinities significantly.

We have undertaken a relativistic configuration-interaction (CI) calculation to investigate the possibility of formation of such metal anions by attachment of an additional $f$ electron to the ground state of thulium and mendelevium. Application of *ab initio* theory shows that at the Dirac-Fock level Tm$^-$ is unbound by 9.29 eV and Md$^-$ is unbound by 4.0 eV, an energy seemingly too large to be recovered by correlation effects, contrary to the expectations of the local-density theory.

Our starting model is the relativistic Dirac-Fock Hamiltonian with the Breit magnetic and retardation corrections treated by first-order perturbation theory. The zeroth-order wave functions are the restricted Dirac-Fock solutions obtained using Desclaux's program [7]. The many-body wave function is first order in form, i.e., it is connected to the zeroth-order function only through configurations generated from single and double excitations into the unoccupied, viz., virtual spinors. For the radial parts of the virtual spinors, we use screened relativistic hydrogenic wave functions; these avoid complications occurring due to variational collapse into the positron sea [8,14]. The effective charge, which is the single adjustable parameter of the virtual spinor, is chosen by minimizing the CI energy eigenvalues subject to the requirement that their average value of $r$ resembles that of the occupied spinor they are replacing.

According to the first-order perturbation theory and prior computational experience, the most important many-body effects are expected to arise from excitations out of the valence space, here mostly the $4f$ electron pairs. To begin with, correlation effects are incorporated by exciting one or two $4f$ electrons into unoccupied spinors which we call virtual spinors. Relativistically, three types of pairs are involved, namely, $(4f_{5/2})^2$, $4f_{5/2}4f_{7/2}$, and $(4f_{7/2})^2$. Based on earlier experience, the pair correlations should be well described through bivirtual excitations into virtual spinors with azimuthal quantum numbers zero through nine where the cutoff is chosen according to the $3l_{\max}$ rule [9,10]. As we can see from Table I however, a cutoff at $l=6$ seems adequate for the current species.

Nonrelativistic practice suggests that one radial function for each symmetry type $(l)$ can account for about 70% of the correlation energy, while two can capture about 90% [9]. Current experience, although limited, suggests relativistic virtual orbitals are at least this effective, when we require $n=l+1$. Since this work is the first application of relativistic CI methods to such complicated angular functions (many $f$ electrons), we have restricted ourselves to one radial function for each

TABLE I. Correlation contributions from bivirtual excitations in Tm and Tm$^-$ (in mhartrees).

| | Tm $[4f^{13}6s^2]$ | | | Tm$^-$ $[4f^{14}6s^2]$ | | |
|---|---|---|---|---|---|---|
| Excitation | $(4f_{7/2})^2$ | $4f_{5/2}4f_{7/2}$ | $(4f_{5/2})^2$ | $(4f_{7/2})^2$ | $4f_{5/2}4f_{7/2}$ | $(4f_{5/2})^2$ |
| $vs^2$ | −0.0180 | | −0.0164 | −0.0380 | | −0.0245 |
| $vp^2$ | −0.2432 | −0.1148 | −0.2196 | −0.4995 | −0.2040 | −0.3277 |
| $vd^2$ | −10.92 | −13.66 | −8.634 | −16.13 | −17.69 | −9.517 |
| $vf^2$ | −66.66 | −140.2 | −45.92 | −91.22 | −149.9 | −44.17 |
| $vg^2$ | −50.12 | −87.23 | −37.20 | −60.43 | −90.34 | −33.73 |
| $vh^2$ | −6.273 | −10.027 | −4.902 | −7.642 | −10.39 | −4.324 |
| $vi^2$ | −1.525 | −2.314 | −1.214 | −1.856 | −2.446 | −1.137 |
| $vsvd$ | −0.0958 | −0.0256 | −0.0871 | −0.1217 | −0.0279 | −0.0831 |
| $vpvf$ | −0.3780 | −0.3280 | −0.3108 | −0.4330 | −0.3877 | −0.2916 |
| $vdvg$ | −0.5771 | −2.323 | −0.6225 | −1.210 | −3.957 | −0.8704 |
| $vfvh$ | −0.7971 | −1.566 | −0.4109 | −1.150 | −1.448 | −0.2144 |
| $vgvi$ | −2.097 | −4.235 | −1.496 | −2.494 | −4.334 | −1.344 |
| $vsvg$ | −0.240 | −0.303 | −0.153 | −0.0388 | −0.0423 | −0.0228 |
| $vpvh$ | −0.0374 | −0.2051 | −0.0225 | −0.0912 | −0.4223 | −0.0418 |
| $vdvi$ | −0.0040 | −0.0182 | −0.0037 | −0.0041 | −0.0167 | −0.0031 |

symmetry type.

For both the neutral atom and the negative ion we find the largest contributions to the correlation energy are from $4f^2 \rightarrow vd^2+vf^2+vg^2$ excitations, which range from a couple of tenths of an electron volt to about 4 eV (Table I). For excitations to crossed virtual spinors such as *vdvg*, *vfvh*, *vpvh*, pairs formed from virtual spinors with $\Delta l=2$ contribute more significantly than those for which $\Delta l=4$ or more. The single excitations $4f \rightarrow vp+vf+vh$ (Table II) and excitations to the hole virtual spinors $(4f_{5/2})^2 \rightarrow 4f_{7/2}(vp+vf+vh)$ (Table III) have also been included but only a modest contribution is observed from them, typically less than 0.1 eV.

When we look at the difference in correlation contributions in the negative ion and the neutral species, electron correlation indeed tends to bind the negative ion, resulting in an overall lowering of the energy gap between the two. However because of heavy cancellations (see following paragraphs), the effect of a particular configuration is no more than a few tenths of an electron volt. Overall, these lowerings are found only to be about 1.3 eV for both thulium and mendelevium, leaving Tm$^-$ and Md$^-$ unbound by 7.9 and 2.7 eV, respectively.

In 1969, Oksuz and Sinanoglu [11] showed to first order, that the nonrelativistic bivirtual energy $E_{vv'}$ for an arbitrary open-subshell atomic state (double excitation into two virtual subshells) could be written as a sum of pair energies ε, which depended solely on the two electron *S*, *L* and the originating subshells, multiplied by coefficients determined entirely by angular restrictions ("group theory"). In two special cases, the contributions to $E_{vv'}$ from two subshells *a* and *b* can be expanded as [9]:

$$E_{vv'}=\frac{O_b}{2(2l_b+1)}\sum_{S,L}(2S+1)(2L+1)\varepsilon(n^a l^a, n^b l^b; SL) ,$$

where either (i) *a* is closed, then $O_b$ is equal to the number of electrons in $n^b l^b$, or (ii) $n^a l^a = n^b l^b$ and there is one electron missing, then $O_b = 4l^a$. In other cases, the general expression [9] should be used. While accuracies have improved since 1969 so that this methodology can no longer be regarded as a first-line computational tool, it can provide important information for analyzing results or diagnosing problems.

If Tm, Md, and their negative ions were nonrelativistic, and first-order perturbation theory were sufficient, we would predict [11,9] using the above formulas that the $f^2$ bivirtual correlation energy in the atom would be exactly 6/7 of that in the negative ion. In fact that is fairly well satisfied, as can be seen from Table I—theory predicts a ratio of 0.8571, while the computed ratio for Tm is 0.8986.

In this work, we have worked out a relativistic variant of the methodology for the purpose of analyzing separately the contributions from the $(f_{5/2})^2$, $f_{5/2}f_{7/2}$, and $(f_{7/2})^2$ bivirtual pair correlations. To do this, we transform a pair of spinors in the uncoupled representation, to the coupled representation in the standard manner [12]:

TABLE II. Correlation contributions from single excitations in Tm and Tm$^-$ (in mhartrees).

| | Tm $[4f^{13}6s^2]$ | | Tm$^-$ $[4f^{14}6s^2]$ | |
|---|---|---|---|---|
| Excitation | $4f_{7/2}$ | $4f_{5/2}$ | $4f_{7/2}$ | $4f_{5/2}$ |
| $vp$ | −0.069 | −0.082 | 0.0 | 0.0 |
| $vf$ | −0.793 | −0.754 | −0.0003 | −0.0002 |
| $vh$ | −1.507 | −1.626 | 0.0 | 0.0 |

TABLE III. Correlation contributions from hole-virtual excitations in Tm (in mhartrees).

| Excitation | Tm $[4f^{13}6s^2]$ $(4f_{5/2})^2$ |
|---|---|
| $4f_{7/2}vp$ | −0.023 |
| $4f_{7/2}vf$ | −0.146 |
| $4f_{7/2}vh$ | −0.116 |

TABLE IV. Relative differences in correlation contributions: dominant effects (in eV).

| | Tm$^-$ [$^1S_0$]−Tm [$^2F_{7/2}$] | | | Md$^-$ [$^1S_0$]−Md [$^2F_{7/2}$] | | |
|---|---|---|---|---|---|---|
| Excitation | $(4f_{7/2})^2$ | $4f_{5/2}4f_{7/2}$ | $(4f_{5/2})^2$ | $(5f_{7/2})^2$ | $5f_{5/2}5f_{7/2}$ | $(5f_{5/2})^2$ |
| $vd^2$ | 0.141 | 0.109 | 0.024 | 0.175 | 0.110 | 0.020 |
| $vf^2$ | 0.668 | 0.264 | −0.047 | 0.435 | 0.415 | 0.012 |
| $vg^2$ | 0.280 | 0.084 | −0.094 | 0.387 | 0.181 | −0.087 |

$$|j_1m_1\rangle|j_2m_2\rangle=(-1)^{j_1-j_2}\sum_{J,M}(-1)^M\sqrt{2J+1}\begin{bmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M\end{bmatrix}|j_1j_2JM\rangle \equiv \sum_J R^J{}_{j_1m_1;j_2m_2}|j_1j_2JM\rangle(M=m_1+m_2) .$$

Following the original work [11], we write the bivirtual pair energy for cases where the Dirac-Fock solution is a single determinant, to first order as

$$E_{vv'}=\sum_J \sum_{n_1,j_1,m_1<n_2,j_2,m_2} |R^J_{j_1m_1;j_2m_2}|^2\varepsilon(n_1j_1;n_2j_2;J) .$$

Note that the "irreducible pair energies" ε in this instance depend on their subshell origins $(nj)$ and the two-electron $J$ only. In effect, this means less separation is possible than in the nonrelativistic case. If we apply this to the current problem, we find that theory predicts that the $(f_{5/2})^2$ bivirtual pair correlation should be the same (ratio of 1); that $f_{5/2}f_{7/2}$ bivirtual pairs in the atom should have 7/8 of the energy of the negative ion and that the $(f_{7/2})^2$ bivirtual pair in the atom should be 3/4 that of the negative ion. From Table I, we find the Tm-to-Tm$^-$ ratios are 1.05, 0.933 (7/8 = 0.875), and 0.765 (3/4 = 0.75), which again are in fair agreement with the theoretical prediction.

The dominant contributions to the energy difference are listed in Table IV. The next most important correlation effects are expected to be those associated with valence space $sf$ pairs (i.e., $4f6s$ pairs in Tm). Based on the nonrelativistic formula for $E_{vv'}$ (above) one might expect their contribution to the electron affinity (increasing it) to be 1/14 of the $sf$ pair energy in the ion. However, the increasing diffusivity of the negative-ion radials may nearly compensate for this, as in Mg$^-$, for example [13]. In the case of the outer $s^2$ pair energy there is only the diffusivity change (occupations are same), and this would tend to decrease (i.e., make less binding) the electron affinity. The most important core-valence pairs are, in Tm, $5p4f$; here the change in occupation (favoring an increased electron affinity) may exceed the decrease due to diffusivity changes. In no case do we expect these contributions to be as large as those from $4f^2$ ($5f^2$ for Md) so both systems should remain unbound.

Correlating $f$ electron pairs poses significant complexity and difficulty in terms of diagonalizing the angular-momentum and energy matrices. To reduce the size of the energy matrix, the relativistic version of the REDUCE procedure has been implemented [10,14]. To illustrate the method, let the reference function be Φ and the original eigenvector set be $\{\chi_i\}$. The first-order matrix element $\langle\Phi|H|\chi_i\rangle$, $i=1,\ldots,N$, can be written

$$C+\sum_k a^kR^k(A,B;C,D) .$$

For most configurations (and all complicated ones) the number ($M$) of radial integrals $R^k(\ )$ (plus the core contribution $C$ if present) is much less than the number ($N$) of the eigenvectors.

The REDUCE method rotates the original basis set $\{\chi_i\}$ to a new orthonormal one $\{Y_i\}$ such that for the first $N-M$ elements, $\langle\Phi|H|Y_i\rangle=0$. These first $N-M$ couplings are then discarded. Due to the large number of determinants encountered here (up to several thousand) from which the $X_i$ are constructed, we introduce here the relativistic Bartlett-Condon-Beck (BCB) method [15] to avoid having to obtain up to several hundred roots of a matrix that can be of order several thousand (e.g., here 300 roots of a matrix of order 2000 may be encountered), a task which is difficult for current diagonalizers.

BCB is based on a 1931 method introduced by Bartlett [16]. The configuration is divided into two (or more) parts. Angular-momentum eigenvectors are obtained for each of the parts, call them $X_{\rm I}$ and $X_{\rm II}$ by diagonalization, for the case of $J=+M_J$. Other $M_J$'s are generated using the step-down operator (to maintain proper phase). The final result is assembled simply as

$$|JM_J\rangle=\sqrt{2J+1}\sum_{M_{J_1},M_{J_2}}\begin{bmatrix} J_1 & J_2 & J \\ M_{J_1} & M_{J_2} & -M_J\end{bmatrix} \times|X_{\rm I}(J_1M_{J_1})\rangle|X_{\rm II}(J_2M_{J_2})\rangle .$$

A code has been written by Beck that does the REDUCE transformation and generates the BCB eigenvectors for configurations interacting with a single Dirac-Fock parent [17]. BCB construction times are negligible, a few seconds on a SparcStation2.

We should also mention that there was a lack of self-consistency in obtaining the multiconfiguration Dirac-Fock solutions [7] for Md and Md$^-$ to the extent of 0.03 a.u. Using a finer mesh and tightening up on energy and normalization tolerances had little effect on the results. Improved self-consistency is obtained using a newer version of the Desclaux code [18]. The size of the inconsistency however is small compared to the energy difference between Md and Md$^-$ and presumably is not going to affect their relative positions significantly. A much better self-consistency is achieved for Tm and $\mathrm{Tm}^-$ ($\approx 0.0004$ a.u.) but a very fine $Z$ extrapolation ($\Delta Z = 0.02$) was needed presumably because $\mathrm{Tm}^-$ is relatively more unbound than $\mathrm{Md}^-$.

If the trends of the local-density calculations [1,2] are to be believed (i.e., that $\mathrm{Tm}^-$ and $\mathrm{Md}^-$ most tightly bind an extra $f$ electron of all the atoms in their respective rows), then we expect that none of the ground-state lanthanides or actinides will accept an extra $f$ electron.

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