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Kinetic energy analysis of atomic multiplets

III. f^m configurations

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Summary. A kinetic energy analysis of total energy differences in atomic multiplets arising from f^m ($m = 2$–12) electronic configurations is performed within the nonrelativistic restricted Hartree–Fock framework. For these 1290 multiplets of 22 lanthanoid (Ce to Er) and actinoid (Th to Fm) atoms, a very good linear correlation between the total energy difference and the kinetic energy difference of the outermost f-electrons is found. The present results, together with our previous ones for the multiplets arising from $s^m p^n$ ($m = 1, 2$; $n = 2$–4) and $s^m d^n$ ($m = 0$–2; $n = 2$–8) electronic configurations, demonstrate that the kinetic energy difference of electrons in open subshells is an excellent predictor of total energy differences among atomic multiplet states.

Key words: Kinetic energy – atomic multiplets – f^m configurations – Hartree–Fock approximation

1 Introduction

Within the nonrelativistic framework for atoms, the Hamiltonian operator $\hat{H}$, the total orbital angular momentum operators $\hat{L}^2$ and $\hat{L}_z$, and the total spin angular momentum operators $\hat{S}^2$ and $\hat{S}_z$ all commute with each other. The corresponding angular momentum quantum numbers L and S are then used to classify the different energy states arising from the same electronic configuration. The classified states are called LS multiplets because, in the absence of an external field, they are $(2L + 1)(2S + 1)$-fold degenerate with respect to the quantum numbers M_L and M_S associated with $\hat{L}_z$ and $\hat{S}_z$, respectively. Hund's famous empirical rules [1] predict the lowest multiplet of a given electronic configuration. However, they do not predict the energy ordering of all the states in a multiplet.

We recently examined [2, 3], at the numerical restricted Hartree–Fock level, how differences in the total energy E correlate with differences in the kinetic energy $T(nl)$ of electrons in specific valence atomic orbitals with quantum numbers nl. Our research covered 115 multiplets arising from the $s^m p^n$ ($m = 1, 2$; $n = 2$–4) electronic configurations of 20 main group atoms [2] and 822 multiplets arising from the $s^m d^n$ ($m = 0$–2; $n = 2$–8) configurations of 27 atoms in groups 2–10 [3]. We found [2, 3] that, despite non-negligible contributions from the core electrons, there is an accurate linear relationship between the kinetic energy difference ΔT of the electrons in open subshells and the total energy difference ΔE. The linear relationship is not universal in that the proportionality constant depends on the identity of the atom and its electronic configuration; moreover, multiplets arising from sd^n configurations had to be classified into groups based on spin multiplicity.

The theoretical underpinning of our kinetic energy analysis of atomic multiplets is the virial theorem [4] which holds exactly for both exact and Hartree–Fock wave functions:

$$E = -T = V/2, \tag{1a}$$

where V is the potential energy. Application of Eq. (1a) to a pair of states gives

$$\Delta E = -\Delta T = \Delta V/2, \tag{1b}$$

which relates the total energy difference to the differences in the components. Equation (1) implies that the total energy E can be analyzed using either of its two components, T or V. Use of the restricted Hartree–Fock model captures the essence of the physics with relatively transparent wave functions. At this level, however, there is no unique decomposition of the potential energy V into orbital contributions because the potential energy operator has a two-electron component. On the other hand, an unambiguous decomposition of the Hartree–Fock kinetic energy T into orbital contributions is trivial since the kinetic energy operator is a one-electron operator. An orbital decomposition is useful because it allows us to focus on the valence electrons in the open subshells that are primarily responsible for the energy differences while ignoring both the core electrons and those valence electrons that do not make an important contribution to the energy differences.

In this work, we round out the picture developed in the previous papers [2, 3] by extending the kinetic energy analysis to atomic multiplets arising from f^m electronic configurations with $m = 2$–12. A total of 1290 multiplet states are examined for 22 atoms from the lanthanoid and actinoid series. We demonstrate an accurate linear correlation between the total energy difference ΔE and the kinetic energy difference $\Delta T(f)$ of electrons in unfilled f-subshells; namely, $\Delta E = -a\Delta T(f)$, where a is a positive constant common to all the multiplets from a chosen configuration of an atom. The Pearson correlation coefficients are greater than 0.999 in most cases. Hartree atomic units are used throughout this paper.

2 Computational details

All our nonrelativisitic, numerical Hartree–Fock calculations were carried out with an enhanced version of the MCHF72 program [5]. The required multiplet energy expressions, in terms of the configuration-average energy E_{av} and Slater's F integrals, were derived from the electrostatic energy formulas of Nielson and Koster [6] with the help of algebraic manipulation software. Tables of these expressions

Table 1. Number of multiplets examined

Z	Atom	Electronic configuration	Number of multiplets
58	Ce	$[\mathrm{Xe}]6s^2 4f^2$	7
59	Pr	$[\mathrm{Xe}]6s^2 4f^3$	17
60	Nd	$[\mathrm{Xe}]6s^2 4f^4$	47
61	Pm	$[\mathrm{Xe}]6s^2 4f^5$	73
62	Sm	$[\mathrm{Xe}]6s^2 4f^6$	119
63	Eu	$[\mathrm{Xe}]6s^2 4f^7$	119
64	Gd	$[\mathrm{Xe}]6s^2 4f^8$	119
65	Tb	$[\mathrm{Xe}]6s^2 4f^9$	73
66	Dy	$[\mathrm{Xe}]6s^2 4f^{10}$	47
67	Ho	$[\mathrm{Xe}]6s^2 4f^{11}$	17
68	Er	$[\mathrm{Xe}]6s^2 4f^{12}$	7
90	Th	$[\mathrm{Rn}]7s^2 5f^2$	7
91	Pa	$[\mathrm{Rn}]7s^2 5f^3$	17
92	U	$[\mathrm{Rn}]7s^2 5f^4$	47
93	Np	$[\mathrm{Rn}]7s^2 5f^5$	73
94	Pu	$[\mathrm{Rn}]7s^2 5f^6$	119
95	Am	$[\mathrm{Rn}]7s^2 5f^7$	119
96	Cm	$[\mathrm{Rn}]7s^2 5f^8$	119
97	Bk	$[\mathrm{Rn}]7s^2 5f^9$	73
98	Cf	$[\mathrm{Rn}]7s^2 5f^{10}$	47
99	Es	$[\mathrm{Rn}]7s^2 5f^{11}$	17
100	Fm	$[\mathrm{Rn}]7s^2 5f^{12}$	7
Total			1290

$[\mathrm{Xe}] = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
$[\mathrm{Rn}] = [\mathrm{Xe}]6s^2 6p^6 4f^{14} 5d^{10}$

are available upon request. Our total energies were convergent to 10 significant figures and various orbital properties to 7 or more significant figures. Errors in the virial ratio V/T were less than 1×10^{-10}, which guarantees the applicability of our basic equations (1a, b).

We chose 22 atoms from the lanthanoid series (Ce to Er) and the actinoid series (Th to Fm) of the periodic table for our analysis of multiplets arising from f^m electronic configurations. The configurations with $m = 1, 13, 14$ were excluded since they lead to only one energy level. The numbers of multiplets examined in this study are summarized in Table 1 for each atom.

We are, of course, aware that relativistic effects can be very important in these heavy atoms. In fact, LS coupling is usually replaced by jj coupling for these atoms. Nevertheless, we think there is conceptual merit in completing this analysis for the entire periodic table using the same model – the nonrelativistic, restricted Hartree–Fock approximation. The simplicity and accuracy of the linear relationship we have found is so striking that we are confident it will be confirmed by relativistic Dirac–Fock calculations for the heavy atoms.

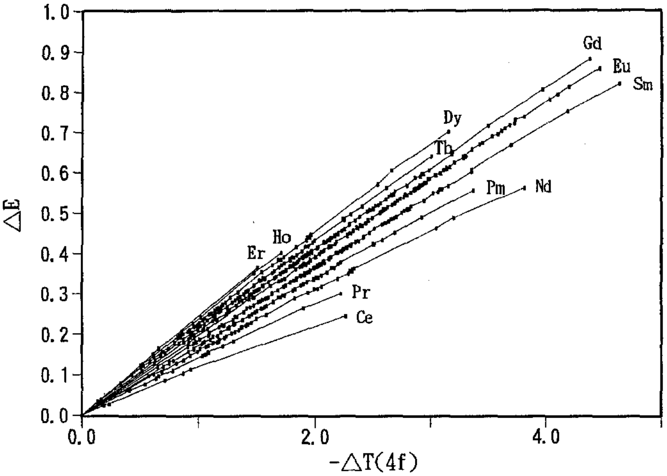

Fig. 1. Linear correlation between ΔE and $-\Delta T(4f)$ for the multiplets arising from the f^m configuration of the lanthanoid atoms Ce through Er

3 Results and discussion

The largest contributions to the kinetic energy come from the core orbitals but the largest contributions to kinetic energy differences among multiplet states come from the valence orbitals. We first examined the relative magnitude of the occupation number weighted orbital kinetic energy difference $\Delta T(nl)$ from various nl orbitals for the 119 multiplets of the Eu atom in the $6s^2\,4f^7$ configuration, where Δ means the difference from the corresponding quantity for the ground state of the same configuration. For all the multiplets, $|\Delta T(4f)|$ was found to be largest. The second largest was $|\Delta T(4d)|$, but it was approximately a third of $|\Delta T(4f)|$. Interestingly, $\Delta T(4f) < 0$ whereas $\Delta T(4d) > 0$; thus these largest two components make opposing contributions to the total $|\Delta T|$.

Based on this pilot study, we examined the correlation between ΔE and $-\Delta T(4f)$ of electrons in the unfilled $4f$ subshell for the 645 multiplets of the 11 lanthanoid atoms from Ce to Er in their $6s^2 4f^m$ electronic configurations. Figure 1 shows that this correlation is surprisingly good for all 11 atoms. We then performed least-squares fits of the data to a simple linear equation,

$$\Delta E = -a\Delta T(4f). \tag{2a}$$

The proportionality constants a and the correlation coefficients R are summarized in Table 2. All the correlation coefficients (except that for Ce) are larger than 0.999, showing that the linear fits are accurate. Although Eq. (2a) gives a good fit, this very definitely does not mean that the kinetic energy differences of the other electrons are negligible. Indeed, all the proportionality constants a are smaller than unity; this implies that there must be opposing contributions from inner electrons (as seen above for the Eu atom) because of Eq. (1b). The proportionality constants a increase with the number m of $4f$ electrons; in fact, they can be roughly approximated

Table 2. Linear correlation between ΔE and $-\Delta T(f)$ of the outermost f electrons for the 1290 multiplets arising from f^m configurations

Z	Atom	a	R
58	Ce	0.11169	0.99669
59	Pr	0.13979	0.99872
60	Nd	0.15457	0.99877
61	Pm	0.16949	0.99958
62	Sm	0.18209	0.99958
63	Eu	0.19523	0.99979
64	Gd	0.20472	0.99981
65	Tb	0.21546	0.99986
66	Dy	0.22595	0.99983
67	Ho	0.23647	0.99982
68	Er	0.24322	0.99984
90	Th	0.11792	0.99566
91	Pa	0.15682	0.99805
92	U	0.18114	0.99818
93	Np	0.20831	0.99927
94	Pu	0.23663	0.99923
95	Am	0.27334	0.99953
96	Cm	0.31461	0.99951
97	Bk	0.38334	0.99962
98	Cf	0.51992	0.99938
99	Es	1.04864	0.99900
100	Fm	− 1.34927	0.99796

by $a = 0.0125m + 0.1016$ for $2 \leqslant m \leqslant 12$ with correlation coefficient 0.988. We are unable to attach much significance to the correlation between a and m except to note that a positive correlation is expected because the occupation weighted contribution of the $4f$ oribtals increases relative to that of the $4d$ orbitals as m increases.

Next, we examined the correlation between ΔE and $-\Delta T(5f)$ for the 645 multiplets arising from $7s^2 5f^m$ configurations of the actinoid atoms from Th to Fm. Figure 2 shows that ΔE correlates very accurately with $-\Delta T(5f)$ in a linear manner. The quality of the correlation is similar to that found above for the lanthanoid atoms. Table 2 lists the results of a regression analysis of the data using a linear formula,

$$\Delta E = -a\Delta T(5f). \tag{2b}$$

The correlation coefficients are again larger than 0.998 for most cases; exceptions are found for Th and Fm. In particular, the Fm atom is a special exception in that its proportionality constant a is negative. This means that ΔE increases with increases in $\Delta T(5f)$ rather than with decreases in $\Delta T(5f)$ as anticipated from Eq. (1a). A finer analysis for Fm shows that $|\Delta T(4f)|$, from the 14 electrons in the filled $4f$ subshell, is larger than $|\Delta T(5f)|$, and $-\Delta T(4f)$ has the expected positive correlation with ΔE. Though the proportionality constants are positive, we have also found that $\Delta T(4f) < \Delta T(5f) < 0$ for Es and $\Delta T(5f) \simeq \Delta T(4f) < 0$ for Cf. Thus the last three atoms in Table 1 do not follow our intuition that the different LS couplings in an open subshell will cause predominant changes in that open

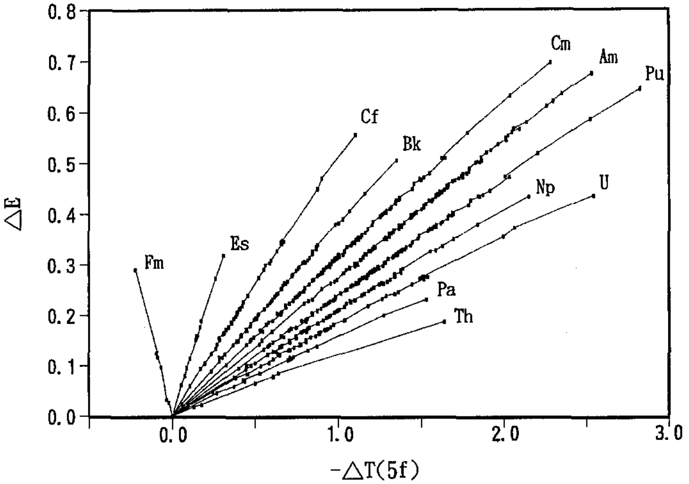

Fig. 2. Linear correlation between ΔE and $-\Delta T(5f)$ for the multiplets arising from the f^m configuration of the actinoid atoms Th through Fm

subshell. Analogous exceptions were also observed previously [3] for $\Delta T(5d)$ and $\Delta T(4d)$ in the $s^2 d^n$ multiplets of Pd and Ir. The physical basis of these exceptions is unclear to us; fine details of this sort may well change if relativistic effects are included.

4 Concluding remarks

Using numerical Hartree–Fock calculations, we have shown that there is a very accurate linear correlation between ΔE and $\Delta T(4f)$ or $\Delta T(5f)$ in 1290 atomic multiplets arising from the f^m electronic configurations of 22 lanthanoid and actinoid atoms. The correlation can be expressed simply by $\Delta E = -a\,\Delta T(f)$ using a single parameter a, which is common to all the multiplets arising from an electronic configuration of an atom. The linear relationships are quite accurate as indicated by correlation coefficients greater than 0.999 in most cases.

In previous papers [2, 3], we demonstrated that there exist accurate linear relationships between the total energy difference ΔE and the kinetic energy difference ΔT of the electrons in open subshells for multiplets arising from $s^m p^n$ and $s^m d^n$ configurations of various atoms.

The previous and present studies show that the ordering of energy levels within a multiplet can be predicted perfectly from the kinetic energy difference of electrons in the open subshells. We are unaware of any other indicator of comparable simplicity and quality for the relative stability of multiplet states. It would be interesting to examine what differences would arise if this study were carried out at the Dirac–Fock level.

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