Interaction with William Carnall

Brian R. Judd*

Henry A. Rowland Department of Physics and Astronomy, The Johns Hopkins University, Bloomberg Center, Baltimore, MD 21218-2686, USA

Abstract

A personal account is given of interaction with William T. Carnall during the period 1977–1988, when I made regular visits to the Argonne National Laboratory to discuss the theoretical background to the spectroscopic work he was carrying out on the lanthanides and actinides.
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1. Introduction

Although I had been aware of the work of William T. Carnall since the early 1960s, it was not until we both attended a conference in 1976 that I got to know him well. The occasion was the Second International Conference on the Electronic Structure of the Actinides, which was held in Wrocław, Poland. Włodzimierz Trzebiatowski and his wife, B. Jeżowska-Trzebiatowska, had nurtured actinide and lanthanide research there since World War II under difficult circumstances. At that conference, Bill and seven collaborators from the Argonne National Laboratory (ANL) presented a paper on crystal-field calculations for 3+ actinides in high-symmetry host crystals [1]. They had previously reported on experimental and theoretical studies of U^{3+} in $LaCl_3$ at the first actinide conference (held in 1974), and that work was extended to all the actinides through Es^{3+}. Their spectroscopic data allowed them to deduce the structures of extensive ranges of energy levels, which could then be fitted parametrically to model Hamiltonians. Two components of these Hamiltonians particularly interested me: the three-electron operators that represented a species of configuration interaction, and the splittings produced by the crystal field acting on the free-ion levels. Some years earlier, I had found that, under some simplifying assumptions, the effects of single-electron excitations to higher configurations could be represented within the f shell by operators acting on three f electrons at a time [2], and I was anxious to learn how the postulated operators performed. I was also interested in seeing how the crystal-field energy levels in the actinides compared to their analogs in the lanthanides. The splittings were roughly twice as large in the actinides [1], a result, no doubt, of the greater penetration into the lattice of the 5f orbitals compared to the 4f. Whatever difficulties the theorist faced in the lanthanides would evidently recur with greater force in the actinides.

The discussion with Bill on these and other topics made it obvious that he and his colleagues were engaged in a major research program. Much of his thinking at that time appears in his classic review article on the aquo-ions of the lanthanides [3]. I agreed to visit ANL the following year, and so began a series of visits that lasted more than a decade. A pattern soon emerged: Bill would write to me outlining some problems that would benefit from some discussion; I would stay at ANL for a few days, in the course of which I would give a lecture on some allied topics and meet with his colleagues. Over the years I kept a notebook reserved for the details of my annual trips to ANL. This is the source of what follows.

*Corresponding author. Fax: +410-516-7239.
E-mail address: juddbr@pha.jhu.edu (B.R. Judd).

2. Correlation crystal fields

At the first of my trips to ANL, which took place in May 1977, Bill asked me to review a preprint that his group had produced in collaboration with Norman Edelstein of LBL (Lawrence Berkeley Laboratory) [4]. It described a parametric energy-level analysis of Ho^{3+}: $LaCl_3$. In spite of an elaborate Hamiltonian, the calculated crystal splitting of the $^3K_8$ level was only 58% of the observed splitting. This confirmed a discrepancy that was first remarked on by Rajnak and Krupke [5]. Several years previously I had myself noticed other 'rogue' levels, such as $^1D_2$ and $^1G_4$ in Pr^{3+}:$LaCl_3$ [6]. Evidently a pure $4f^N$ configuration combined with a conventional one-electron crystal field was not adequate. A correlation crystal field (CCF), comprising multi-electron operators, was needed to represent the effects of excited configurations. Unfortunately, a formal development of even the simplest CCF (merely involving two-electron operators) requires a large number of new parameters, so some simplifications had to be envisaged. Bill and his colleagues John Morrison and Paul Fields were among the first to introduce two-electron crystal-field operators to an actual physical example (namely, Pr^{3+}:$LaCl_3$), but limited their orbital ranks k to just $k = 2$ [7]. For Ho^{3+}, on the other hand, components for which $k = 6$ seemed to be important [4]. Assigning slightly different radial wavefunctions to the spin-up (A) and spin-down (B) electrons takes the standard one-electron crystal-field Hamiltonian towards a full-blown CCF approach in a very modest way. In fact, a mere doubling of the number of parameters occurs [8,9]. In discussions with Bill, I decided to see how this idea could be applied to ^3K of Ho^{3+} $4f^{10}$. Although two ^3K terms occur in f^{10}, an approximate wavefunction of the observed ^3K term can be obtained by coupling six A electrons in an F state to four B electrons in an I state. One would expect the attractive exchange forces for electrons with similarly oriented spins to contract their radial wavefunctions, and this idea leads to a negative value for the coefficient c_6 describing the strength of the CCF. However, for ^3K of f^{10}, the calculation of the standard one-electron crystal-field operator $U^{(6)}$ involves the factor (1453–1485), the 1453 coming from the I component and the 1485 from the F. This almost perfect cancellation makes the final result very sensitive to CCF and other effects. In particular, electron transfer into the f shell from the ligands can lead to positive c_k [10]. That is evidently what is needed for Ho^{3+}, as was realized later [11].

Other sources for the CCF were discussed with Bill at that first visit to ANL in 1977. These included the effects of ligand polarizations by the f electrons and a double delta-function interaction involving pairs of electrons located on particular ligands [12]. Many of these ideas have remained in play over the years. Recent work has taken advantage of the octahedral symmetries exhibited by elpasolite crystals, for which excitations of the type $f \leftrightarrow p$ have been established as the most important [13,14].

3. Hypersensitive pseudoquadrupole transitions

In May 1978, I received a letter from Bill stating that several recent developments had increased his interest in the mechanisms of hypersensitivity in the lanthanides, and that he would like to discuss these matters when I visited ANL that year. Some years earlier, Christian Klixbüll Jørgensen and I had described the strange hypersensitivity to environment of certain lanthanide absorption bands that obey the selection rules for electric quadrupole radiation [15]. We ascribed this phenomenon to the inhomogeneity of the dielectric. However, in his letter, Bill called my attention to some extremely strong quadrupole bands for $NdCl_3$ and $ErCl_3$ in the vapor phase [16]. Their strengths far exceeded those of the typical aquo ions. I could see at once that an explanation was available if the trichlorides had a pyramidal rather than a planar structure. Unlike the situation for an aquo ion, a strong electric field coming from the halide ions would be acting at a lanthanide site. Although this would necessarily vanish at the lanthanide nucleus (for otherwise the nucleus would move to a new equilibrium position), it could mix orbitals of opposite parity into the f orbitals. These hybrid orbitals, when acted on by the electric vector of the radiation field, would lead to quadrupole selection rules via a mechanism that I had previously described [17].

Bill's letter also called my attention to what appeared to be a new source for the hypersensitivity: dynamic coupling. An f electron on a lanthanide ion produces induced dipoles on the ligands, which, in the absence of a center of inversion, combine to yield an extended dipole moment that can interact strongly with the radiation field [18]. The inhomogeneous-dielectric mechanism, on the other hand, envisages the radiation field forcing the dipoles it induces in the ligands to sympathetically pulsate, thereby emitting radiation that will have a strong quadrupole component in view of the close proximity of the ligands to the lanthanide ion. As a result of Bill's questioning, I worked out the details of both mechanisms and found them to be merely two different verbalizations of the same mathematics [19]. Douglas Newman had suspected as much in a private communication to me some years earlier.

Both mechanisms involve the ligand polarizability, and Bill wondered if it might be profitable to explore a relationship between the value of the quadrupole strength Ω_2 and the polarizability α of the ligands. This seemed a good idea to me at the time, and I went so far

as to write that a paper with Bill was in preparation [19]. This plan turned out to be frustrated by the difficulty of describing parametrically the various ligand structures that we wanted the theory to encompass, and no joint article was produced. Bill's desire to bring lanthanide and actinide intensities under a single overarching theme was nevertheless fulfilled in a lengthy article presented in 1984 at the First International Symposium on Rare Earths Spectroscopy in Wrocław [20]. Among the many other contributions on intensities at that conference was that of Steven Mason and Brian Stewart, who extended their dynamic-coupling model to include ligand anisotropies.

4. Orthogonal operators

A major part of Bill's interest centered on how best to fit experiment to theory. For energy levels, the obvious procedure was to make a least-squares fit. As additional parameters are included, it usually happens that those already found change their values slightly. To minimize this phenomenon, the parameters should be uncorrelated. To achieve this, the operators whose strengths are specified by the parameters need to be orthogonal [21]. This is easy to achieve if the operators are labelled by the irreducible representations (IRs) of various Lie groups, such as the groups SO(7), G_2 and SO(3) used by Racah to separate parts of the inter-electronic Coulomb interaction [22]. The only difficulty is that some operators may have the same group labels, an example being the three-electron operator t_2 [2] and the two-electron operator e_3 of Racah, both of which share the same set of IRs, namely, (220)(22)0. Hannah Crosswhite, a colleague of Bill's, brought this problem to my attention. She had constructed a computer program to handle all f-electron configurations, and it was being widely circulated informally. It was easy enough to find the linear combination of e_3 and t_2 that is orthogonal to e_3: the answer was given in 1984 [23]. It was at about that time that my interest was awakened in the unexpected zeros and proportionalities exhibited by Hannah's matrix elements [24]. Group theory revealed an insignificant error [25], which was corrected when tables of the matrix elements were finally published [26]. The three-electron operators t_i became a subject for sporadic discussion over the years. It is thanks to Bill's enthusiasm that their analysis was pursued as vigorously as it was.

5. Later interests

After a hiatus of a few years, I resumed my visits to ANL in 1982. Bill was still interested in the environment of an actinide or lanthanide ion, and pondered what differences might emerge if there was a change from 8-fold to 9-fold coordination. He was becoming interested in actual numerical calculations of such matters as overlap integrals (using the code of Bob Cowan). Hank Crosswhite also became involved in adjusting the Hartree–Fock procedures to correct the large discrepancies (of roughly 30% or more) in the Slater integrals. I was happy to discuss these developments but I had no special expertise in these areas.

A topic nearer my heart arose in 1983, when Bill called my attention to a preprint by Mike Reid and Fred Richardson dealing with the effect of anisotropic ligands on optical transitions in Eu^{3+} [27]. I was able to set the theory out in a formal way using spherical tensors, and the analysis was included in a review article I wrote some years later [28]. Bill's interest in intensities continued in 1984, when he speculated in a letter to me that free-ion parameters could still be useful in the analysis of U^{4+} in $ThBr_4$. This led me to think about error distributions in fitting energy levels to experiment using orthogonal operators. It appeared that normal distributions should not be expected. Further analysis of orthogonal operators as well as some anomalies in electronic Raman scattering were studied in 1985. All kinds of questions were raised in the following years. These included whether the total intensity of transitions of the type $f^{13} \to f^{12}d$ would be 13 times as intense as those for $f \to d$, all things being equal. (The answer turned out to be yes.) This led to a general formula for the oscillator strengths for transitions of the type $4f^N \to 4f^{N-1}5d$, as exemplified by $N = 6$ and 8 [29]. I had the opportunity to report on this at the 1987 Lisbon meeting, where Bill was also in action. He was involved with two presentations, one on the laser-induced fluorescence of Bk^{4+} in CeF_4, the other on the crystal-field analysis of various lanthanides in LaF_3 assuming an approximate C_{2v} site symmetry. The subject of approximate symmetries was a subject he often brought up in our discussions.

6. Remembrance

My continual interaction with Bill Carnall over the years was a source of stimulation for my own research and kept me in touch with experimental f-electron spectroscopy. Bill's disarming forthrightness and intellectual integrity made it a pleasure to discuss matters with him. His influence went far beyond the ANL campus. His visits to colleagues in Poland were much valued. It was only in last June, at a workshop on rare earths at Lądek Zdrój, that a tree, planted in his honor by the side of a stream near the conference site, was pointed out to me. Ironically, the week of the conference coincided with the date of his death. We conferees regretted his absence without being aware of that

tragedy. Fortunately, he will live on in the memories of his family, his colleagues, and his friends.

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