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Important Correlation Effects for the  $\text{Er}^{3+} 4f^{11}$   
 $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$  Laser Transition Energy

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Abstract

Most of the important correlation effects transitions within the  $4f^n$  manifold of rare earth atomic ions are identified as coming from three sources:  $4f^2$  pair correlations, single excitations from the valence shell and shallow core, and pair excitations where both of the electrons go into the incomplete  $4f$  subshell (exclusion effects). A method (REDUCE) of managing the large basis sets encountered is discussed. Relativistic Configuration Interaction calculations are done to obtain the energy of the laser transition (in, e.g. GaN)  $\text{Er}^{3+} ^4\text{I}_{15/2} \rightarrow ^4\text{S}_{3/2}$ , to which correlation contributes  $\sim 4000 \text{ cm}^{-1}$ . The residual error of  $864 \text{ cm}^{-1}$  may be due to missing second order effects, and to truncation of the angular basis.

Keywords: Er IV spectra, correlation, relativity, configuration interaction, *ab initio*

# I. INTRODUCTION

This article is dedicated to Professor Per-Olov Löwdin who did so much for quantum physics and chemistry over many decades. The author particularly remembers all his efforts in creating and maintaining the “Sanibel” conferences, which is one of the few venues where atomic, molecular, and solid state computationalists routinely interact.

Over the past decade or so, we have been developing a Relativistic Configuration Interaction (RCI) methodology capable of accurate predictions of a variety of properties such as electron affinities, hyperfine structure, Landé  $g$  values, and transition probabilities. Our applications have been to the atomic transition metal states  $(d + s)^n p^m$  with  $n + m < 5$  ( $m = 0, 1$ ). The occupancy limit was imposed because, at the time, for larger values the calculations were simply computationally too involved. Transition metals have considerable technological importance, in atomic form to plasma physics (as impurities), in astrophysics (abundances), and in condensed matter, e.g. in catalysis, deep traps in semi-conductors, as potential hydrogen storage devices, etc. In a “spirit of Sanibel”, it is the author’s contention – due to the localized nature of  $d$  (and  $f$ ) electrons – that much atomic knowledge of transition metals can be helpful in condensed matter calculations involving localized properties of transition metals. Specifically, the important configurations ( $N$ -electron basis functions) and localized radial functions should make a suitable modified appearance in condensed matter problems.

Recently we have extended our methodology to treat  $(d + s)^n p^m$  configurations with  $n + m < 8$  and  $m = 0, 1$  in Tc I [1], of possible interest to Atomic Trap Trace Analysis (ATTA) experimental studies [2]. There is a dramatic growth in the complexity (number of vectors, determinants and coefficients) of the correlation functions with the occupancy of  $d$  (or  $f$ ) electrons. In Table I, we illustrate this for the important correlation manifold, created by removing two electrons from  $(d + s)^n$  and replacing them with two  $f$  electrons. Table II exhibits the growth for another important correlation manifold, formed by removing two electrons from  $f^n$  and replacing them with two  $l > 2$  electrons.

In addition to our recent work on more complicated transition metal atomic states, we believe our methodology has become powerful enough to do *ab initio* calculations on rare earth ions of medium complexity. Our attention was recently drawn to the potential importance of  $\text{Er}^{3+}$  transitions in a GaN host to high temperature optoelectronic device applications [3]. This application involves transitions within  $4f^{11}$ . Since lifetimes are typically of the order of a several ms [4,5], crystal field effects dominate the lifetimes, and in fact semi-empirical calculations exist for both lifetimes and spectra [6] which are in good agreement with experiment. Yet these fitted parameters provide little insight into what are the important correlation effects in the wavefunctions. In this work we seek to answer this question. Just as it is expected that the atomic spectra of  $\text{Er}^{3+}$  in  $\text{LaCl}_3$  deviates little from that of  $\text{Er}^{3+}$  [7], we expect the important atomic correlation effects will also be important in the crystal. Finally, the *ab initio* work of Cai *et al* [8] on the  $4f^2$  levels of  $\text{Pr}^{3+}$  and our work on  $f^{13}$  and  $f^{14}$  [9] serve as a useful starting point as to what types of configurations might be important.

## II. METHODOLOGY

Our approach [10] is fully relativistic and begins with the Dirac-Coulomb (-Breit) Hamiltonian. A reference wavefunction is generated for the  $4f^{11}$  manifold by solving [11] the Multi-Configurational Dirac-Fock equations. The reference is chosen to provide a good starting point for generation of the correlated wavefunction. Our remarks concerning what constitutes a “good” correlation function are governed by what is achievable in *ab initio* calculations for  $d^n$  ( $f^n$ ) states, today.

Initially, a first order form is chosen for the correlated wavefunction, which means we include only single and double subshell excitations from the reference function. As in usual in cases of low to medium ionicity, the Dirac and Coulomb operators are sufficient to determine the form of the correlation function. Subshells unoccupied in the reference function are represented with spinors formed from a product of a (to be determined) radial function (or “virtual”) and relativistic hydrogenic angular factors which are eigenstates of  $\kappa$ ,  $j_z$ , and relativistic parity. Relativistic screened ( $Z^*$ ) hydrogenic (RSH) functions are used to represent the virtual. This choice allows easy variation of the virtual while applying the energy variational principle, and avoids variational collapse into the positron sea. Both major and minor components are determined at once, and the  $Z^*$  is varied around an estimated value determined by matching the  $\langle r \rangle$  of the virtual and the subshell it is replacing. Our single particle expansions have the characteristic property of acquiring much (up to 90%) of the correlation in a single RSH, but exhibit much slower convergence after that. Usually, 2-3 RSH per symmetry ( $l, j$ ) are needed per shell ( $\langle r \rangle$ , and hence  $Z^*$ , is shell dependent). Viewed differently, our virtuals are representing the compact portion of the Rydberg and continuum series associated with the specific configuration. Due to the nature of the Coulomb operator (large when  $r(i, j) \sim 0$ ) and perturbation theory (electron density maximized when  $\langle r \rangle$  of the virtual and its replacement are similar), only the compact portion of these series are essential.

Based on past experience [8,9,12], for the  $4f^{11}$  manifold, we expect the following three

types of correlation effects to be important: (1)  $nl \rightarrow v(l+2)$ , (2)  $nl n'l' \rightarrow 4f xl''$  and (3)  $4f^2 \rightarrow vl v'l'$ . In this work, we shall restrict  $n$  ( $n'$ ) to 4 or 5 only. Category 2 excitations are known as exclusion effects. When  $(n, n') = (4, x = n'')$  they are complex preserving excitations. These correlation effects are expected to be differentially large; i.e. to be large and also significantly  $J$  dependent. For the first two excitations, perturbation theory restricts the virtual's  $l$  (major component) to  $< 10$ . Computationally it has been found that this restriction can also be applied to the third excitation.

Currently, *ab initio* atomic energy matrices for multi-root  $d^n$  ( $f^n$ ) states are limited to order 20 000 or lower [10,13]. Two advantages ensue from this restriction (1) the non-zero matrix elements may be held in memory. This is not a major advantage, as the bulk ( $\sim 70\%$ ) of CPU time is spent in construction of matrix elements, and not diagonalization, (2) “small” matrices yield wavefunctions easier to interpret and use. The latter is particularly relevant for  $f$  values, where non-orthonormality effects would be included, if present, which can be done by using the methods of King *et al* [14] or Löwdin [15].

On the other hand, the 20 000 limit is a restrictive one, as can be judged from Tables I and II. Within a first order wavefunction form, the order barrier can be reduced following an initial suggestion by Bunge [16], and implemented by ourselves over the past two decades. This recognizes that the matrix element  $\langle \Phi | H | \chi \rangle$  where  $\Phi$  ( $\chi$ ) is the reference (correlation) manifold is expressible as a linear combination of a number ( $M$ ) of radial integrals. For  $d^n$  ( $f^m$ ) states,  $M \ll N$ , the number of eigenvectors in a correlation manifold. To limit  $M$ , we assume the radial functions are independent of  $j$ . We do retain full flexibility in the reference function; i.e. no specific linear combination of the  $R$  relativistic eigenvectors within  $\Phi$  is assumed (we have a multi-reference treatment). One is then able to rotate the original  $X$  basis to form a new basis  $Y$ , with  $N - M \times R$  vectors which yield a zero matrix element with  $\Phi$ . These can be discarded in the context of a first order form. Tests on Zr II [17] yielded errors  $< 200 \text{ cm}^{-1}$  which is of the same order as other correlation manifolds or moderate second order effects which are not included either.

Each of the REDUCE [17] survivors produced by the rotation ( $Y$  basis) is expanded in

the full set of determinants for that manifold. This increases costs of assembling the energy matrix element structure (see Table II); i.e. a listing of coefficients and radial integral labels which allows evaluation of the energy matrix elements, once the radial integrals are known. Some efficiency is gained by grouping the determinants in each vector by relativistic configuration. Configurations are then tested to determine whether any interaction can occur, thus alleviating the need to test all pairs of determinants to see whether they interact. A structure file is valuable because it allows one to vary  $Z^*$  without reassembling the structure (which is  $\sim 70\%$  of CPU costs), or to shift diagonal matrix elements to “represent” second order effects (see next section), or to reuse structure of an earlier calculation, in the process of building up the  $N$  electron basis. The total number of coefficients could exceed 100 million; for the present calculation, only  $\sim 2$  million occur.

### III. APPLICATION

Four transitions in  $\text{Er}^{3+}$  implanted in GaN have been observed by Thaik *et al* [3]. They are  ${}^4\text{I}_{15/2} \rightarrow {}^4\text{F}_{7/2}$ ,  ${}^4\text{I}_{15/2} \rightarrow {}^2\text{H}_{11/2}$ ,  ${}^4\text{I}_{15/2} \rightarrow {}^4\text{S}_{3/2}$  and  ${}^4\text{I}_{15/2} \rightarrow {}^4\text{F}_{9/2}$ . We performed MCDF calculations for the  $4f^{11}$  manifold [11] for these, and found the largest energy difference error was  $+5174 \text{ cm}^{-1}$  for the third transition, so we focused on that.

A series of 2 manifold calculations ( $4f^{11}$  with a correlation manifold) were done, for the purpose of determining which configurations were differentially important, and determining the best value of  $Z^*$  for a single RSH. This gave us a means of qualitatively judging the combined effects of missing second order manifolds and incomplete virtual sets, within the single RSH approximation. Significantly different  $Z^*$  for two differentially important manifolds would indicate the need to use two RSH for this virtual in the combined matrix, for example.

Examination of work on  $f^{13}$ ,  $f^{14}$  [9] and  $\text{Pr}^{3+}$   $4f^2$  [8] suggests that we may restrict  $l < 7$ . In the categories of excitations listed in the last section, two manifold calculations were done for each of the following (excitation from  $4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{11}$ ): Category (1),  $nl \rightarrow v(l+2)$ :  $4f \rightarrow vp + vf + vh + vk$ ;  $4p, 5p \rightarrow 4f + vf$ ;  $4d \rightarrow vd + vg + vi$ ;  $4s, 5s \rightarrow vd$ . In Category (2),  $nl n'l' \rightarrow 4f x l''$ , we examined:  $(4p + 5p)^2 \rightarrow 4f^2$ ,  $(3d + 4d)^2 \rightarrow 4f^2$ ,  $4f vf$ ;  $4s 4d \rightarrow 4f^2$ ;  $4s 5s \rightarrow 4f^2$ . As excitations like  $5p^2 \rightarrow 4f^2$  were small, ‘‘companion’’ excitations like  $5p^2 \rightarrow 4f vf$  were not examined. The excitations  $4s^2, 5s^2 \rightarrow 4f^2$  do not produce  $J = 3/2$  or  $15/2$ .

In category (3),  $4f^2 \rightarrow vl v'l'$ , we examined  $4f^2 \rightarrow vs^2 + vp^2 + vd^2 + vf^2 + vg^2 + vh^2 + vi^2 + vs vd + vp vf + vd vg + vf vh + vg vi + vs vg + vs vi$ . For all three categories, only a modest number of manifolds differentially contributed more than  $100 \text{ cm}^{-1}$  to the energy difference. These were:  $4f^2 \rightarrow vd^2 + vf^2 + vg^2$ ;  $4d^2 \rightarrow 4f^2$ ;  $4f \rightarrow vf + vh$ ;  $5p \rightarrow 4f + vf$ ;  $4d \rightarrow vg$ ;  $4p \rightarrow 4f + vf$  and  $4s \rightarrow vd$ . A single data set was constructed from these, for each  $J$ , and the energy matrix diagonalized. Computation costs were about 1 hour on a SUN Ultra30 ( $\sim 250 \text{ MHz}$ ) for the  $J = 3/2$  matrix. Inclusion of the magnetic part of the Breit

operator would increase this  $\sim 4$  times. These effects, if differentially important, should be mainly confined to the  $4f^{11}$  manifold. A separate calculation yielded an increase of  $309 \text{ cm}^{-1}$ , due to the magnetic Breit operator. This is nearly compensated by (two manifold) differential contributions from  $4f^2 \rightarrow vh^2$  and  $3d^2 + 3d \ 4d \rightarrow 4f^2$  correlation ( $-264 \text{ cm}^{-1}$ ). The net result, correlation plus magnetic Breit, is an energy difference of  $19412 \text{ cm}^{-1}$  as compared to the experimental one [7] derived from  $\text{Er}^{3+}:\text{LaCl}_3$  of  $18290 \text{ cm}^{-1}$ , yielding an error of  $864 \text{ cm}^{-1}$  ( $\sim 0.11 \text{ eV}$ ).

An analysis of the contribution of each correlation manifold's contribution to the energy difference is shown in Table III. These are obtained from a single calculation (all important manifolds), using intermediate normalization. Writing  $\Psi = \Phi + \sum_i \chi(i)$  with the conditions that  $\langle \Phi | \Phi \rangle = 1$  and  $\langle \Phi | \chi \rangle = 0$ , each correlation manifold may be assigned an energy contribution of  $[C(i)/C(\Phi)] \langle \Phi | H | \chi(i) \rangle$  which appears in columns 2 and 3 of Table III. Here  $C(\Phi)$  is the coefficient of the reference function, and  $C(i)$  the coefficient of the correlation function, as determined by energy diagonalization. This assignment is a first order one only, as the value of  $C(i)$  is obtained through diagonalization of the energy matrix, and so also includes effects of higher order.

How can one account for the  $864 \text{ cm}^{-1}$  error? Comparing columns 4 and 5 of Table III, we see this is about the loss of energy in going from the two to all manifolds calculation. This may suggest that missing second order effects are responsible for most of the difference, especially for  $5s \rightarrow vd$ ,  $4d \rightarrow vg$  and  $4d^2 \rightarrow 4f^2$ . The important triple (quadruple) excitations are likely formed [18] by unlinked products of large single (pair) and pair excitations. For Table III, the largest of the pair excitations are  $4f^2 \rightarrow vf^2 + vg^2$ . Thus for  $5s \rightarrow vd$  ( $4d \rightarrow vg$ ) we would need to add manifolds  $5s \ 4f^9 \ vd \ (vf^2 + vg^2)$  [ $4d^9 \ 4f^9 \ vg \ (vf^2 + vg^2)$ ] and for  $4d^2 \rightarrow 4f^2$ , to add manifold  $4d^9 \ 4f^{11} \ (vf^2 + vg^2)$ . This last also corresponds to (from  $4f^{11}$ )  $4d^2 \rightarrow vf^2 + vg^2$  which would require inclusion of  $4d^6 \ 4f^{13} \ (vf^2 + vg^2)$ , or  $4d^2 \rightarrow vf^2 + vg^2$  from  $4f^8 \ 4f^{13}$ , and perhaps others. All these manifolds are even more complicated than those in a first order (form) function. At least a few of them could be included in an *ab initio* manner, by applying REDUCE, using portions of the first order

(form) function as reference, as we have done in the past [19]. These references should themselves be REDUCE vectors, in order to keep their number as low as possible.

Some estimate of these effects can be made by appealing to perturbation theory. Second order correlation energy contributions have the form  $-H(i,0)^2/(H(i,i) - H(0,0))$ . In our first order (form) calculation, we preferentially correlate  $|0\rangle$ , the reference function, at the expense of  $|i\rangle$ , the correlation function. This increases  $H(i,i) - H(0,0)$ , increasing the second order energy. By artificially shifting  $H(i,i)$ , by approximately the amount of correlation energy in  $H(0,0)$ , or  $-.330$  a.u. in this case (see Table III), an estimate of second order effects may be obtained. For properties other than energy differences, the shift is adjusted to yield a match to the observed energy spectra [20]. For  $\text{Er}^{3+}$ , this shift applied to  $4f \rightarrow vf$ ,  $5s \rightarrow vd$  and  $4d^2 \rightarrow 4f^2$  lowered the correlation energy for  $J = 3/2$  -138, -89, and  $-37 \text{ cm}^{-1}$  respectively, only a moderate effect, which is likely to be even smaller, differentially.

For the  $4f \rightarrow vf$ ,  $5s \rightarrow vd$ , and  $4d \rightarrow vg$ , the completeness of the virtual set was examined, as a potential source of error. It was necessary to add a second  $vf$  (included in Table III), but one  $vd$  and  $vg$  was found to be adequate. Finally,  $3d \rightarrow vg$  excitations were examined in a separate calculation; their effect was to increase the error  $+85 \text{ cm}^{-1}$ . There is also some error associated with the angular truncations employed.

At present, there seem to be two ways to considerably improve the efficiency of *ab initio* calculations for  $d^n$  ( $f^n$ ) states, recognizing that most ( $> 70\%$ ) computational cost occurs from structure assembly. The first is to divide this task over several processors, which is trivial to do, given the processors. We did this in the mid 1990's in our U-/U calculations [21]. The second is useful when there is more than one virtual of a given symmetry. Structure can be reused then. As a simple illustration, consider correlating  $1s^2$  with  $vp^2$  and  $xp^2$ . Once the matrix element  $\langle vp^2|H|vp^2\rangle$  is assembled,  $\langle xp^2|H|xp^2\rangle$  trivially follows by appropriately changing "principle" quantum numbers. We used this non-relativistically [22], to lower computation times by factors of 4.

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TABLE I. Illustrating  $N$ -electron Basis Set Growth with Number of Electrons for  $(d+s)^{n-2} vl^2$  <sup>a</sup>.

| Label               | # MCDF <sup>b</sup> | Full | Reduce <sup>c</sup> | RF <sup>d</sup> | Comments     |
|---------------------|---------------------|------|---------------------|-----------------|--------------|
| $(d+s)^5 J = 5/2$   | 29                  | 333  | 111                 | 3.0             | Max $J$ (e)  |
| $(d+s)^6 J = 3$     | 29                  | 723  | 116                 | 6.2             | Near Max $J$ |
| $(d+s)^7 J = 5/2$   | 29                  | 1068 | 121                 | 8.8             | Max $J$      |
| $(d+s)^8 J = 3$     | 15                  | 1289 | 65                  | 19.8            | Near Max $J$ |
| $(d+s)^3 p J = 1$   | 40                  | 83   |                     |                 | Ta II [10]   |
| $(d+s)^4 p J = 7/2$ | 87                  | 653  | 321                 | 2.0             | Near Max $J$ |
| $(d+s)^5 p J = 3$   | 145                 | 1963 | 558                 | 3.5             | Max $J$      |
| $(d+s)^6 p J = 7/2$ | 155                 | 4248 | 620                 | 6.9             | Tc I         |
| $(d+s)^7 p J = 3$   | 145                 | 6382 | 602                 | 10.6            | Max $J$      |
| $(d+s)^8 p J = 5/2$ | 99                  | 6891 | 424                 | 16.3            | Max $J$      |

<sup>a</sup>Number of eigenvectors needed (fixed  $J_z = J$ ) for the pair correlation where two  $d/s$  electrons are replaced by two  $f$  electrons. Includes three manifolds. Under almost all circumstances, this is a key contributor to the differential correlation energy.

<sup>b</sup>Number of eigenvectors (fixed  $J_z = J$ ) in the  $d^M$ ,  $d^{M-1}s$ , and  $d^{M-2}s^2$  configurations ( $M = n + 2$ ).

<sup>c</sup>Application of the REDUCE can decrease the number of eigenvectors (FULL) to this number, with little energy loss ( $\sim 200 \text{ cm}^{-1}$ ), but produces bigger eigenvectors (more determinants). This is a way to greatly cut down the size of the energy matrix, at some expense of having more complicated energy matrix elements.

<sup>d</sup>RF = Full/Reduce.

<sup>e</sup>The  $J$  displayed is that for which <sup>b</sup> is maximum (or near max).

TABLE II. Growth of Basis Set with  $n$  for  $4f^{n-2} vl^2$  <sup>a</sup>.

| $n$ | $J^b$ | $N_r^c$ | $N_f^d$ | $N_R^e$ | $N_d^f$ | $N_c^g$ |
|-----|-------|---------|---------|---------|---------|---------|
| 3   | 4.5   | 7       | 27      | 27*     | 119     | .003M   |
| 4   | 4.0   | 19      | 151     | 76      | 841     | .064M   |
| 5   | 4.5   | 29      | 524     | 116     | 3018    | 0.35M   |
| 6   | 5.0   | 37      | 1317    | 148     | 7530    | 1.1M    |
| 7   | 5.5   | 42      | 2513    | 168     | 13739   | 2.3M    |
| 8   | 5.0   | 37      | 3627    | 148     | 22393   | 3.3M    |
| 9   | 5.5   | 26      | 4135    | 104     | 23517   | 2.4M    |

<sup>a</sup>This correlation manifold must be included for  $l = 2, 3, 4$  for  $4f^n$  reference manifolds. For  $n > 9$ , columns  $N_f$  and  $N_d$  may be obtained from  $4f^{16-n} vg^2$  and column  $N_r$  from  $4f^{14-n}$  (same  $J$ ).

<sup>b</sup> $J$  corresponding to maximum value of  $N_f$ .

<sup>a</sup> $N_r = \#$  of  $4f^n$  eigenvectors for this  $J$ .

<sup>a</sup> $N_f = \#$  of  $4f^{n-2} vl^2$  eigenvectors for this  $J$ .

<sup>a</sup> $N_R = \#$  of REDUCE eigenvectors for  $4f^{n-2} vl^2 = 4 \times N_r$  (valid for  $l > 2$ ); \* = no reduction possible.

<sup>a</sup> $N_d = \#$  of determinants in the  $4f^{n-2} vg^2$  basis for  $l = 4$ . The actual number is somewhat less; i.e.  $M_J$  for  $vg^2 < 7$ .

<sup>a</sup> $N_c =$  total  $\#$  of coefficients in REDUCE manifold for  $4f^{n-2} vg^2 (= N_R \times N_d)$ . In millions (M).

TABLE III. Correlation Energy Contributions (EC in meV) to the  $4f^{11} J = 3/2 - J = 15/2$  Energy Difference ( $\Delta E$  in  $\text{cm}^{-1}$ ).

| Excitation <sup>a</sup> | EC (meV) |         | $\Delta E$ ( $\text{cm}^{-1}$ ) |                  |
|-------------------------|----------|---------|---------------------------------|------------------|
|                         | EC(15/2) | EC(3/2) | Full <sup>b</sup>               | Two <sup>c</sup> |
| $4f \rightarrow vh$     | -90      | -142    | -415                            | -459             |
| $4f \rightarrow vf$     | -70      | -105    | -282                            | -361             |
| $4f^2 \rightarrow vd^2$ | -542     | -568    | -210                            | -260             |
| $4f^2 \rightarrow vf^2$ | -4737    | -4768   | -250                            | -292             |
| $4f^2 \rightarrow vg^2$ | -3563    | -3656   | -750                            | -768             |
| $5p \rightarrow f$      | -718     | -1327   | -491                            | -522             |
| $5s \rightarrow vd$     | -56      | -116    | -484                            | -656             |
| $4d \rightarrow vg$     | -2285    | -2138   | +1186                           | +969             |
| $4d^2 \rightarrow 4f^2$ | -46      | -221    | -1412                           | -1699            |
| $4p \rightarrow f$      | -46      | -183    | -1105                           | -1033            |
| Total                   |          |         | -4213                           | -5081            |

<sup>a</sup>From  $4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{11}$ .

<sup>b</sup>All excitations +  $4f^{11}$  together.

<sup>c</sup> $4f^{11}$  + 1 excitation.