

University of Nebraska - Lincoln

DigitalCommons@University of Nebraska - Lincoln

Anthony F. Starace Publications

Research Papers in Physics and Astronomy

January 1974

Effect of virtual 4d-shell excitations on rare earth spectra

Anthony F. Starace

University of Nebraska-Lincoln, astarace1@unl.edu

Follow this and additional works at: <https://digitalcommons.unl.edu/physicsstarace>



Part of the [Physics Commons](#)

Starace, Anthony F., "Effect of virtual 4d-shell excitations on rare earth spectra" (1974). *Anthony F. Starace Publications*. 163.

<https://digitalcommons.unl.edu/physicsstarace/163>

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Anthony F. Starace Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Submitted July 26, 1973.

Effect of virtual 4d-shell excitations on rare earth spectra

Anthony F. Starace

Department of Physics, Imperial College, London SW7, and Behlen Laboratory of Physics, University of Nebraska–Lincoln, Lincoln, Nebraska 68508

Abstract

Ab initio energies for electric dipole transitions $4d^{10}(^1S_0) \rightarrow 4d^9 4f$ $J = 1$ in triply-ionized lanthanum have been calculated by constructing an effective interaction, acting within the configuration $4d^9 4f$, that incorporates effects of virtual 4d-shell excitations to all orders of perturbation. Virtual 4d-shell excitations, included within the random phase approximation, and virtual excitations to singly-excited configurations $4d^9 \epsilon f$ are found to reduce the ordinary electrostatic interaction by 38% for the 1P_1 term of $4d^9 4f$, by 6% for the 3D_1 term, and by 3% for the 3P_1 term. The relevance of this calculation to rare earth spectroscopy generally is discussed, with particular regard to the usual theoretical problem that calculated term energies are much larger than experimental ones. Present results are in good agreement with experiment and greatly improve upon previous theoretical work.

1. Introduction

A well known difficulty in rare earth spectroscopy is that theoretically predicted term levels for a given configuration are invariably spread over a larger energy range than is observed experimentally (Wybourne 1965). Neglect of configuration interaction between the given configuration and other, highly excited configurations is generally supposed to be the root of the problem. It is only recently however that serious efforts have been made to account for such configuration interaction, within the framework of perturbation theory carried to second order by Newman and Taylor (1971) and to third order by Morrison and Rajnak (1971). While these theoretical calculations have been successful in predicting term energies which are in better agreement with experiment, they are nevertheless quite complex since they require explicit consideration of a very large number of configurations. In this paper we employ an alternative, non-perturbative theoretical approach based upon a formal partitioning of the hamiltonian to study the spectrum of allowed term levels of the optically excited La IV configuration $4d^9 4f$. Rather than dealing explicitly with highly excited configurations, we instead single out a class of interactions that are summed to all orders to produce an effective hamiltonian for this configuration. The three allowed term levels for this configuration are obtained simply as the three eigenvalues of the 3×3 effective hamiltonian matrix. Except for the substitution of reduced effective interactions for the larger zero-order interactions, this method for obtaining spectral levels of a given configuration is identical in form to that presented long ago by Condon and Shortley (1935). For the simple optically excited configuration studied here our calculations give absolute transition energies that are in good agreement with experiment.

The motivation for studying triply-ionized lanthanum is provided by earlier theoretical work of the author and collaborators. The spectrum of the optically allowed transitions $4d^{10} \rightarrow 4d^9 4f$ in La IV is the simplest of the 4d-shell photoabsorption spectra of rare earth metal films observed experimentally by Zimkina *et al.* (1967), Fomichev *et al.* (1967), and Zimkina and Gribovskii (1971), and by Haensel *et al.* (1970), and Gudat and Kunz (1972). (Recently Trebbia and Colliex [1973] have observed similar spectra in experiments studying electron-impact excitation of the $4d^{10}$ shell in rare earth metals.) These complex spectra were interpreted by Dehmer *et al.* (1971) as resulting from a simple two step process, namely, photoexcitation of a 4d electron into the 4f shell, *i.e.*, $4d^{10} 4f^N \rightarrow 4d^9 4f^{N+1}$, followed by autoionization of the optically allowed term levels of $4d^9 4f^{N+1}$, *i.e.*, $4d^9 4f^{N+1} \rightarrow 4d^9 4f^N + e^-$. Furthermore, the allowed term levels of the configuration $4d^9 4f^{N+1}$ were interpreted to be spread over an energy range of ~ 20 eV due to an unusually large exchange interaction. The justification for this simple theory is provided by the independent particle model, which shows that, due to a potential barrier, the 4d and 4f wavefunctions overlap in coordinate space very well, whereas the 4d wavefunction and those of higher energy f-orbits hardly overlap at all. Thus the only way (within the independent particle model) to ionize a 4d electron is to excite it to a 4f-orbit, from which it can leak out to continuum f-orbits and, to a lesser extent, continuum p-orbits. Also, because of the excellent overlap between 4d and 4f wavefunctions, exchange interaction is very large for the $4d^9 4f^{N+1}$ configuration.

The general theory for the above two-step process has been given by Starace (1972). Term level spectra for several $4d^9 4f^{N+1}$ configurations have been calculated by Sugar (1972). Also, oscillator strengths or autoionization line profiles for the optically allowed La $4d^9 4f$ term levels have been calculated by Dehmer and Starace (1972). In these three papers, two main approximations were made: (1) In computing term levels for the configurations $4d^9 4f^{N+1}$, Sugar (1972) reduced *ab initio* interaction integrals by about 33%. This procedure, which was also adopted by Dehmer and Starace (1972), substituted for a detailed consideration of configuration interaction. In the absence of this "scaling factor," the calculated term levels would be much more widely spaced than is experimentally observed. As pointed out at the beginning of this Introduction, this is a common problem in rare earth spectroscopy. (2) Virtual excitations from the 4d-shell were recognized as being potentially important by Starace (1972) and Dehmer and Starace (1972), but were not otherwise treated.

For the special case of La IV, this paper shows that approximations (1) and (2) above are intimately related. Using the random phase approximation to account for the virtual excitation of 4d electron pairs, we obtain an effective, *reduced* interaction acting in the space of the La $4d^9 4f$ configuration. *Ad hoc* reduction of the zero-order interaction by about 33% is no longer necessary to obtain term levels that are in good agreement with experiment. In simplest terms, the relevance of this paper to the physics of the rare earths is to point out that all processes, real and virtual, whose matrix elements involve the overlap of 4d and 4f wavefunctions should probably be included in any calculation involving the 4f electrons, preferably to all orders of perturbation theory.

As to the generality of the lanthanum results presented here, let it first be said that the importance of virtual core excitations has only recently been discovered in atomic physics: Amusia (1971), Amusia *et al.* (1971), and Wendin (1971, 1972, 1973) have found, using the random phase approximation, that virtual core excitations have far from negligible effects on the photoionization cross sections of the rare gases. Based on our results for lanthanum presented here, we predict for the rare earths generally that virtual 4d-shell excitations will strongly reduce the interaction between 4f-electrons. The simple configuration La $4d^9 4f$ is chosen here both for com-

parison with the calculation of Dehmer and Starace (1972) and also because, since this configuration has only a single electron outside an almost-closed shell, it is a straightforward matter to use the random phase approximation for constructing the effective interaction.

Other rare earth configurations, however, will require different approximations for constructing the effective interaction, even though the important interactions are deemed to be the same, or similar, in all cases. For example, the other excited, triply-ionized rare earth configurations of the form $4d^9 4f^{N+1}$, in which there are a number of equivalent $4f$ electrons, will require a modified random phase approximation. The paper by Rowe (1968) may be helpful for this case. Another example is the calculation of the term levels for the ground state, triply-ionized lanthanide configurations $4d^{10} 4f^N$. In this case the effect of virtual $4d$ -excitations on the interactions between $4f$ -electrons may perhaps be accounted for by a procedure analogous to that used in nuclear spectroscopy (Kuo and Brown 1966). Lastly, as pointed out by Dehmer *et al.* (1971), these considerations for $4d$ -shell excitations in the rare earths should apply also to the $3p$ -shell excitation spectra in the transition metals observed experimentally by Sonntag and Haensel (1969).

2. The partitioned hamiltonian

The properties of a partitioned hamiltonian have been discussed at length by Feshbach (1958) and Löwdin (1962). A main property of the partitioned hamiltonian is that it enables a simple derivation of Rayleigh-Schrödinger and Brillouin-Wigner forms of perturbation theory, even in the degenerate case. However, it also serves as the starting point for more sophisticated forms of perturbation theory, such as in Brandow's (1967) derivation of a linked-cluster Bloch-Horowitz expansion for energies and wavefunctions of open-shell nuclei. In particular, it serves as a useful framework when the residual interaction, or perturbation, is strong and finite-order perturbation methods converge slowly (Brandow 1967).

We first split the exact hamiltonian H into a zero-order hamiltonian, from which a complete set of electron orbital wavefunctions can be obtained, and a residual interaction :

$$H = H_0 + V.$$

We approximate an exact state $|E\rangle$, *i.e.*, $H|E\rangle = E|E\rangle$, by a set of N states $|i\rangle$, each of which is a linear combination of Slater determinants constructed with the single electron orbital wavefunctions of H_0 . Defining the projection operator

$$P \equiv \sum_{i=1}^N |i\rangle \langle i|$$

the initial approximation to $|E\rangle$ is

$$|\psi_E\rangle \equiv P|E\rangle = \sum_{i=1}^N |i\rangle \langle i|E\rangle$$

The brackets $\langle i|E\rangle$ are a set of unknown coefficients whose determination gives the desired solution for $|\psi_E\rangle$. If the set of states $|i\rangle$ are well-chosen, then $\sum_i |\langle i|E\rangle|^2 \lesssim 1$.

By introducing the complementary projection operator $Q \equiv 1 - P$, which includes all states of the system not included in P , one can formally solve the Schrödinger

equation for $|\psi_E\rangle$ (Feshbach 1958, Löwdin 1962):

$$\{PH_0P + PVP + PVQ [Q(E - H)Q]^{-1} QVP\} |\psi_E\rangle = E|\psi_E\rangle \quad (1)$$

Furthermore, we can define a reaction matrix,

$$\mathcal{V}(E) \equiv V + VQ [Q(E - H)Q]^{-1} QV \quad (2)$$

which may be shown to satisfy the integral equation (Löwdin 1962):

$$\mathcal{V}(E) = V + VQ (E - H_0)^{-1} \mathcal{V}(E) \quad (3)$$

The Schrödinger equation for may thus be written :

$$\{PH_0P + P\mathcal{V}(E)P\} |\psi_E\rangle = E|\psi_E\rangle. \quad (4)$$

The hamiltonian for $|\psi_E\rangle$ thus is defined entirely within the model subspace of states in P . Effects due to states in Q on the subspace P are implicitly included in the reaction matrix $\mathcal{V}(E)$, obtained from either equation (2) or (3). Note that $\mathcal{V}(E)$ depends on the *exact* energy E , and thus in practice one must iterate to obtain the correct eigenvalues E and eigenstates $|\psi_E\rangle$. That is, the eigenvalue spectrum of the $N \times N$ matrix $\{PH_0P + P\mathcal{V}(E)P\}$ depends on the value E used to construct $\mathcal{V}(E)$. If one of the eigenvalues happens to equal E , then that eigenvalue and its eigenvector solve the Schrödinger equation (4). The solutions of the partitioned Schrödinger equation (4) are thus, in general, not orthogonal, since they are solutions of different hamiltonians (one for each energy E).

As for the interaction between states in P , we note that $P\mathcal{V}(E)P$ consists of two terms. The first term is the ordinary interaction PVP acting in the model subspace. The second term represents a modification of the interaction between states in P due to states in Q . If the states in P are low-energy states and those in Q are all higher-energy states, then the effect of the second term is to *reduce* PVP . In any particular calculation good judgement is needed both in choosing the model subspace P and in obtaining a suitable approximation for the “effective” interaction $P\mathcal{V}(E)P$. There is no simple prescription.

3. Effective interaction within the La IV configuration 4d⁹4f $J = 1$

We take up now the problem of obtaining the transition energies for the electric dipole transitions $4d^{10}(^1S_0) \rightarrow 4d^94f J = 1$ in triply-ionized lanthanum. That is, we want to obtain the energy levels of the optically allowed terms of the configuration 4d⁹4f relative to the energy of the ground state 4d¹⁰. There are three allowed terms: 1P_1 , 3D_1 , and 3P_1 . For our model hamiltonian H_0 , we choose that of Herman-Skillman (1963). For our model subspace P , we choose the three Slater determinant states

$$\begin{aligned} |^1P\rangle &\equiv |1s^2 \dots 4d^9 4f 5s^2 5p^6(^1P_1)\rangle \\ |^3D\rangle &\equiv |1s^2 \dots 4d^9 4f 5s^2 5p^6(^3D_1)\rangle \\ |^3P\rangle &\equiv |1s^2 \dots 4d^9 4f 5s^2 5p^6(^3P_1)\rangle. \end{aligned} \quad (5)$$

These three states are degenerate in energy. Relative to the ground state configuration $4d^{10}$, their energy is $\omega_0^{\text{HS}} = 3.7994$ au. Further discussion of these zero-order states is given by Dehmer and Starace (1972).

As emphasized in the Introduction, we base our calculation here on the assumption that a major contribution to $PV(E)P$ is provided by those electrostatic interactions that involve the overlap of $4d$ and $4f$ wavefunctions. Such overlap will occur when the configuration $4d^9 4f$ interacts with (i) multiply-excited configurations such as $4d^7 4f^3$, $4d^7 4f^2 \epsilon f$, $4d^5 4f^5$, etc., and also with (ii) singly-excited continuum configurations $4d^9 \epsilon f$. Such overlap will also occur if we assume the initial configuration $4d^{10}$ is correlated, in which case the configuration $4d^9 4f$ and the configurations in (i) and (ii) may be reached from the virtually excited states $4d^8 4f^2$, $4d^8 4f \epsilon f$, etc., by electric dipole transitions.

In what follows we construct the electrostatic part of $PV(E)P$ in two stages. (Spin-orbit interaction will be considered later.) First we employ the random phase approximation to compute an effective interaction that includes the effects of *multiple* excitations from the $4d$ -shell. This effective interaction, however, will be defined in the extended model space P' consisting of all *singly*-excited f -orbitals, i.e., $4d^9 4f$, $4d^9 5f$, \dots , $4d^9 \epsilon f$, \dots . As a second step, we then reduce the model space to that defined in (5) above, by considering the further modification of the effective interaction within the configuration $4d^9 4f$ due to the singly-excited configurations $4d^9 5f$, \dots , $4d^9 \epsilon f$, \dots . This second step has been discussed by Starace (1972) and was employed in the calculation of Dehmer and Starace (1972). Because of the effect of the potential barrier on the relative strength of electric dipole and electrostatic matrix elements (Dehmer *et al.* 1971), we ignore $4d \rightarrow p$ transitions as well as virtual excitations from closed shells other than $4d$.

3.1. The random phase approximation for the effective interaction

The importance of the interactions included in the random phase approximation (RPA) was first demonstrated in atomic physics by Altick and Glassgold (1964), who obtained improved agreement with experiment for excitation energies, oscillator strengths, and photoionization cross sections of the alkaline earth metal elements. Fano and Cooper (1968) have discussed the import of this approximation for atomic physics, and recently Amusia *et al.* (1971) and Wendin (1971, 1972, 1973) have achieved outstanding success in calculating the photoionization cross sections of the rare gases with this approximation. The RPA has, of course, been used for a long time in other branches of physics. Therefore we shall discuss but not derive the standard RPA equations and refer the interested reader to the thorough textbook derivations of Brown (1971) and of Fetter and Walecka (1971).

We consider the closed shell system $\text{La IV } 1s^2 \dots 4d^{10} 5s^2 5p^6 ({}^1S_0)$ to be our shell model reference configuration, whose Slater determinant we denote by $|0\rangle$. Excitation of a single electron from the reference configuration is equivalent, in the language of many-body theory, to creating a "particle-hole pair." For example, a state of the shell model configuration $4d^9 4f$ would be denoted by $a_n^\dagger b_a^\dagger |0\rangle$, where the operator a_n^\dagger , "creates a particle" with quantum numbers $n \equiv 4f m_l m_s$, and b_a^\dagger "creates a hole" with quantum numbers $a \equiv 4d m_l m_s$. (Note that in this paper we use Roman letters to denote quantum numbers and Greek letters to denote hole quantum numbers.) Similarly, the operators $b_a a_n = (a_n^\dagger b_a^\dagger)^\dagger$ "destroy" the particle-hole pair a_n , i.e., $b_a a_n a_n^\dagger b_a^\dagger |0\rangle = |0\rangle$. The advantage of this many-body language is that one deals with operators, such as $a_n^\dagger b_a^\dagger$, rather than with whole configurations. A main example is the random phase approximation, which in simplest terms limits itself to the consideration of interactions between particle-hole pairs.

The equations-of-motion derivation of the RPA, which we invoke below, is particularly suitable for optical spectra. The equations-of-motion referred to are those equations that result from taking the commutators of the particular-hole creation and destruction operators, $a_n^\dagger b_a^\dagger$, and $b_a a_n$, with the exact hamiltonian. The reasoning behind the random phase approximation to these equations is as follows. For a closed-shell system we define the *exact, correlated* ground state by $|\psi^{(0)}\rangle$. Similarly, we denote an *exact, correlated* state produced from $|\psi^{(0)}\rangle$ by the absorption of a photon of energy ω by $|\psi^{(\omega)}\rangle$. Now the electric dipole transition operator can only excite or de-excite a single electron. The random phase approximation to the equations of motion is the assumption that the *only* way to reach $|\psi^{(\omega)}\rangle$ from $|\psi^{(0)}\rangle$ is to either excite or de-excite a *single* particle-hole pair. Formally, one takes the matrix element of the equations-of-motion for $a_n^\dagger b_a^\dagger$ and for $b_a a_n$ between the states $|\psi^{(\omega)}\rangle$ and $|\psi^{(0)}\rangle$ and keeps only those matrix elements of the form $\psi_{an}^{(\omega)} \equiv \langle \psi^{(\omega)} | a_n^\dagger b_a^\dagger | \psi^{(0)} \rangle$ and $\varphi_{an}^{(\omega)} \equiv \langle \psi^{(\omega)} | b_a a_n | \psi^{(0)} \rangle$.

At this point it should be clear why the RPA has not been as widely used in atomic physics as in other branches of physics. In dealing with the amplitudes $\psi_{an}^{(\omega)}$ and $\varphi_{an}^{(\omega)}$, one loses sight of initial and final configurations. For example, if the quantum numbers an refer to a hole in the 4d shell and a particle in the 4f shell, then $\psi_{an}^{(\omega)}$ is the probability amplitude for producing the excited state $\langle \psi^{(\omega)} |$ by means of a $4d \rightarrow 4f$ transition from the correlated ground state $|\psi^{(0)}\rangle$. All of the configuration space transitions $4d^{10} \rightarrow 4d^9 4f$, $4d^8 4f^2 \rightarrow 4d^7 4f^3$, $4d^8 4f \epsilon' f \rightarrow 4d^7 4f \epsilon \epsilon' f$, etc., contribute to the amplitude $\psi_{an}^{(\omega)}$. Similarly, all of the configuration space transitions such as $4d^8 4f^2 \rightarrow 4d^9 4f$, $4d^8 4f \epsilon f \rightarrow 4d^9 \epsilon f$, $4d^6 4f^4 \rightarrow 4d^7 4f^3$, etc., contribute to the amplitude $\varphi_{an}^{(\omega)}$. However, in the absence of virtual excitations from the 4d-shell (and ignoring other closed shells) $\varphi_{an}^{(\omega)} = 0$, since then $|\psi^{(0)}\rangle$ would be the uncorrelated shell-model reference state $|0\rangle$. In this case we can make the following definite statement: if $|\psi^{(0)}\rangle = |0\rangle$, then $|\psi^{(\omega)}\rangle$ would be restricted to some linear combination of singly-excited shell model states, i.e., $4d^9 4f$, $4d^9 5f$, . . . , $4d^9 \epsilon f$. . . (ignoring p-orbits). Thus, $\varphi_{an}^{(\omega)}$ is a measure of the strength of virtual, multiple 4d-shell excitations.

Without further ado, we write down the equations one obtains, by the method discussed above, for the RPA amplitudes and $\psi_{an}^{(\omega)}$ and $\varphi_{an}^{(\omega)}$ (Fetter and Walecka 1971):

$$(-\omega + \epsilon_n - \epsilon_a) \psi_{an}^{(\omega)} + \sum_{\beta m} (U_{an, \beta m} \psi_{\beta m}^{(\omega)} + \bar{U}_{an, \beta m} \varphi_{\beta m}^{(\omega)}) = 0 \quad (6a)$$

$$(-\omega - \epsilon_n + \epsilon_a) \varphi_{an}^{(\omega)} - \sum_{\beta m} (U_{an, \beta m} \varphi_{\beta m}^{(\omega)} + \bar{U}_{an, \beta m} \psi_{\beta m}^{(\omega)}) = 0 \quad (6b)$$

where the interactions between the particle-hole pairs an and βm are given in terms of matrix elements of the electrostatic interaction, $V \equiv 1/r_{12}$:

$$U_{an, \beta m} \equiv (-1)^x (\langle -\beta n | V | m - \alpha \rangle - \langle -\beta n | V | -\alpha m \rangle) \quad (7a)$$

$$\bar{U}_{an, \beta m} \equiv (-1)^x (\langle nm | V | -\alpha - \beta \rangle - \langle -nm | V | -\beta - \alpha \rangle) \quad (7b)$$

with

$$x \equiv (l_a + m_l^\alpha) + (1/2 + m_s^\alpha) + (l_\beta + m_l^\beta) + (1/2 + m_s^\beta).$$

$U_{an, \beta m}$ represents the scattering of one particle-hole pair state, βm , into another, an . $\bar{U}_{an, \beta m}$, on the other hand, represents either the simultaneous excitation or de-excitation of two particle-hole pairs an and βm by means of the electrostatic interaction. The phase x arises from the requirement that the hole operators b_a and b_a^\dagger transform

under rotations as tensor operators (Fetter and Walecka 1971). Lastly, the matrix element of V may be written in terms of Slater integrals R^K by making the usual multipole expansion:

$$\begin{aligned} \langle -\beta n | V | m - \alpha \rangle &= \sum_{K,q} (-1)^{q+m_\beta+m_n} \langle l_\beta l_n || V_K || l_m l_\alpha \rangle \begin{pmatrix} l_m & K & l_\beta \\ m_m & q & m_\beta \end{pmatrix} \begin{pmatrix} l_\alpha & K & l_n \\ -m_\alpha & -q & -m_n \end{pmatrix} \\ &\times \delta(-m_{s'}^\beta, m_s^m) \delta(m_{s'}^n, -m_s^\alpha) \end{aligned} \quad (8)$$

where

$$\begin{aligned} \langle l_\beta l_n || V_K || l_m l_\alpha \rangle &= ([l_\beta][l_n][l_m][l_\alpha])^{1/2} \begin{pmatrix} l_\beta & K & l_m \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_n & K & l_\alpha \\ 0 & 0 & 0 \end{pmatrix} R^K(\beta n, m \alpha) \\ R^K(\beta n, m \alpha) &= \int_0^\infty \int_0^\infty dr_1 dr_2 P_{nl(\beta)}(r_1) P_{nl(n)}(r_2) \frac{r_1^K}{r_2^{K+1}} P_{nl(m)}(r_1) P_{nl(\alpha)}(r_2) \end{aligned}$$

and $[x] \equiv 2x + 1$.

In this paper we use the Herman-Skillman (1963) model potential, which is a local approximation to the non-local Hartree-Fock potential. We thus ignore certain terms not included in equation (6) (Altick and Glassgold 1964), which, however, are identically zero for the Hartree-Fock potential. Our aim in approximating the Hartree-Fock potentials is to reduce the computational labor necessary to generate a complete set of wavefunctions for lanthanum.

We proceed now to couple the particle-hole pairs into states of well defined angular momentum L and spin S . Define

$$\psi_{an}^{(\omega)LS} \equiv \sum_{\text{all } m} (LM_L | l_\alpha m_l^\alpha l_n m_l^n) (SM_S | 1/2 m_s^\alpha 1/2 m_s^n) \psi_{an}^{(\omega)} \quad (9a)$$

$$\varphi_{an}^{(\omega)LS} \equiv (-1)^{L+M_L+S+M_S} \sum_{\text{all } m} (LM_L | l_\alpha m_l^\alpha l_n m_l^n) (SM_S | 1/2 m_s^\alpha 1/2 m_s^n) \varphi_{an}^{(\omega)} \quad (9b)$$

where the phase factor in equation (9b) is necessary to make $\varphi_{an}^{(\omega)LS}$ a double tensor of ranks L and S , and where the symbols $(LM_L | l_\alpha m_l^\alpha l_n m_l^n)$, etc., are Clebsh-Gordan coefficients. Multiply equation (6a) from the left by the Clebsh-Gordan coefficients in equation (9a), and multiply equation (6b) from the left by the phase factor and coefficients in equation (9b). Summing over all m_l and $m_{s'}$ so that now the subscripts α, n, β , and m indicate only the principal and orbital angular momentum quantum numbers, we obtain:

$$(-\omega + \epsilon_n - \epsilon_\alpha) \psi_{an}^{(\omega)LS} + \sum_{\beta m} (U_{an,\beta m}^{LS} \psi_{\beta m}^{(\omega)LS} + \bar{U}_{an,\beta m}^{LS} \varphi_{\beta m}^{(\omega)LS}) = 0 \quad (10a)$$

$$(-\omega - \epsilon_n + \epsilon_\alpha) \varphi_{an}^{(\omega)LS} - \sum_{\beta m} (U_{an,\beta m}^{LS} \varphi_{\beta m}^{(\omega)LS} + \bar{U}_{an,\beta m}^{LS} \psi_{\beta m}^{(\omega)LS}) = 0 \quad (10b)$$

where

$$U_{an,\beta m}^{LS} \equiv (-1)^{l_n+l_m} \left(\frac{2\delta_{S0}}{[L]} \langle l_\beta l_n || V_L || l_m l_\alpha \rangle - \sum_K (-1)^{K+L} \begin{pmatrix} l_\alpha & l_\beta & K \\ l_m & l_n & L \end{pmatrix} \langle l_\beta l_n || V_K || l_\alpha l_m \rangle \right) \quad (11a)$$

and

$$\begin{aligned} \bar{U}_{an,\beta m}^{LS} \equiv & (-1)^L + S(-1)^{l_n + l_m} \left(\frac{2\delta_{S0}}{[L]} \langle l_n l_m || V_L || l_a l_\beta \rangle \right. \\ & \left. - \sum_K (-1)^{K+L} \begin{Bmatrix} l_\beta & l_n & K \\ l_a & l_m & L \end{Bmatrix} \langle l_n l_m || V_K || l_\beta l_a \rangle \right) \end{aligned} \quad (11b)$$

The diagonal elements $U_{an, an}^{LS}$ give the term dependence of the particle-hole electrostatic energy listed in Condon and Shortley (1935, p 299).

Equations (10) may be simplified by using abstract operator notation and regarding $\psi_{an}^{(\omega)LS}$ and $\phi_a^{(\omega)LS}$ as components of vectors $\psi^{(\omega)LS}$ and $\phi^{(\omega)LS}$:

$$(-\omega + H_0) \psi^{(\omega)LS} + (U^{LS} \psi^{(\omega)LS} + \bar{U}^{LS} \phi^{(\omega)LS}) = 0 \quad (10'a)$$

$$(-\omega - H_0) \phi^{(\omega)LS} - (U^{LS} \phi^{(\omega)LS} + \bar{U}^{LS} \psi^{(\omega)LS}) = 0 \quad (10'b)$$

H_0 is the model hamiltonian, whose matrix elements are :

$$(H_0)_{an,\beta m} = (\epsilon_n - \epsilon_a) \delta_{nm} \delta_{a\beta}. \quad (12)$$

Using equation (10'b) to eliminate $\phi^{(\omega)LS}$ in equation (10'a), we obtain the following equation for the amplitudes $\psi^{(\omega)LS}$:

$$(H_0 + \mathcal{V}^{LS}(\omega)) \psi^{(\omega)LS} = \omega \psi^{(\omega)LS} \quad (13a)$$

which has an effective interaction $\mathcal{V}^{LS}(\omega)$ between particle-hole pairs :

$$\mathcal{V}^{LS}(\omega) \equiv U^{LS} - \bar{U}^{LS} \left(\frac{1}{\omega + H_0 + U^{LS}} \right) \bar{U}^{LS}. \quad (13b)$$

This effective interaction, which has been derived diagrammatically by Brandow (1967, p. 806), has two terms. The first, U^{LS} , represents the ordinary interaction between singly- excited closed shell configurations. The second term vanishes if $\phi^{(\omega)LS}$ is zero, and hence represents the effects of virtual, multiple excitations from closed shells. $\mathcal{V}^{LS}(\omega)$ depends slightly on the photon energy ω , which appears in the denominator of the second term.

3.2. Reduction of the model space

The effective electrostatic interaction $\mathcal{V}^{LS}(\omega)$ between particle-hole pairs is, in configuration space, the effective interaction between the singly-excited configurations $4d^9 4f$, $4d^9 5f$, \dots , $4d^9 \epsilon f$, \dots . We wish now to reduce this model space to obtain the effective electrostatic interaction within the configuration $4d^9 4f$. In what follows, we identify the configuration $4d^9 4f$ by "4f" and the other excited configurations $4d^9 \epsilon f$ by " ϵf ." Integrations over ϵ are understood to include summation over the discrete states starting with $4d^9 5f$.

Starace (1972) shows, following the method of Fano (1961), that the modification of the electrostatic interaction within the configuration $4d^9 4f$ due to virtual excitations to other singly-excited configurations $4d^9 \epsilon f$ is described by a second-order, energy-dependent term :

$$F_{4f,4f}^{LS}(\omega) \equiv \mathcal{P} \int d\epsilon \mathcal{V}_{4f,\epsilon f}^{LS}(\omega) \frac{1}{\omega - (\epsilon - \epsilon_{4d})} \mathcal{V}_{\epsilon f,4f}^{LS}(\omega) \quad (14)$$

Note, however, that in equation (14) we employ the effective interaction $\mathcal{V}^{LS}(\omega)$ rather than the ordinary electrostatic interaction. The symbol \mathcal{P} indicates that the Cauchy principal value is to be taken when integrating over the singularity that occurs when the zero-order transition energy $(\epsilon - \epsilon_{4d})$ equals the photon energy ω .

In summary, the transition energy ω for the electric dipole transition $4d^{10} \rightarrow 4d^9 4f$ ($2S + 1L$) in triply-ionized lanthanum (in the LS -coupling approximation) is given by :

$$\omega = \omega_0^{\text{HS}} + \mathcal{V}_{4f,4f}^{LS}(\omega) + F_{4f,4f}^{LS}(\omega) \quad (15)$$

where $\omega_0^{\text{HS}} \equiv (\epsilon_{4f} - \epsilon_{4d}) = 3.7994$ au, $\mathcal{V}_{4f,4f}^{LS}(\omega)$ is the diagonal matrix element of equation (13b) for the particle-hole configuration $4d^9 4f$, and $F_{4f,4f}^{LS}(\omega)$ is the diagonal matrix element given by equation (14). For each LS -term, equation (15) must be solved self-consistently to obtain ω since both $\mathcal{V}^{LS}(\omega)$ and $F^{LS}(\omega)$ depend on ω . The effect of spin-orbit interaction is discussed in the next section.

The numerical procedures required for these calculations are quite ordinary, except perhaps for equation (13b), which is solved in two steps. First one obtains the matrix $K^{LS}(\omega)$, defined by

$$K^{LS}(\omega) \equiv \left(\frac{1}{\omega + H_0 + U^{LS}} \right) \bar{U}^{LS} \quad (16)$$

as the solution of the set of linear equations :

$$\sum_{\beta m} (\omega + H_0 + U^{LS})_{\alpha n, \beta m} K_{\beta m, \gamma p}^{LS}(\omega) = \bar{U}_{\alpha n, \gamma p}^{LS} \quad (17)$$

$\mathcal{V}_{4f,4f}^{LS}(\omega)$ is then obtained from substitution of $K(\omega)$ in equation (13b):

$$\mathcal{V}_{4f,4f}^{LS}(\omega) = U_{4f,4f}^{LS} - \sum_{\beta m} \bar{U}_{4f, \beta m}^{LS} K_{\beta m, 4f}^{LS}(\omega) \quad (18)$$

where $\beta m = 4f, 5f, \dots, \epsilon f, \dots$

4. Energies for transition to the states $|^1P_1\rangle$, $|^3D_1\rangle$, and $|^3P_1\rangle$

The 3×3 interaction matrix between the LS -coupled states $|^1P_1\rangle$, $|^3D_1\rangle$, $|^3P_1\rangle$ defined in (5) is formed as follows. The total effective electrostatic interaction is diagonal in LS -coupling, and its matrix elements as well as those of the model hamiltonian are given by equation (15). The spin-orbit interaction is non-diagonal and thus both mixes the term levels and alters the transition energies slightly from those obtained from equation (15). We use spin-orbit parameters with the following values, which were provided by Dr. J. Sugar (private communication):

$$\zeta_{4d} = 1.2 \text{ eV, and } \zeta_{4f} = 0.07981 \text{ eV.}$$

The 3×3 interaction matrix thus formed was diagonalized for a range of photon energies ω . The three eigenvalues are denoted by $E_\gamma(\omega)$, where γ indicates their approximate LS -term designation, and are plotted against ω in Figure 1. Also plotted in Figure 1 is the diagonal line $y = \omega$. The intersection of $y = E_\gamma(\omega)$ with $y = \omega$ gives the position of the desired transition energy for each term γ . That is, the transition energy for the γ term is that energy ω which satisfies $E_\gamma(\omega) = \omega$.

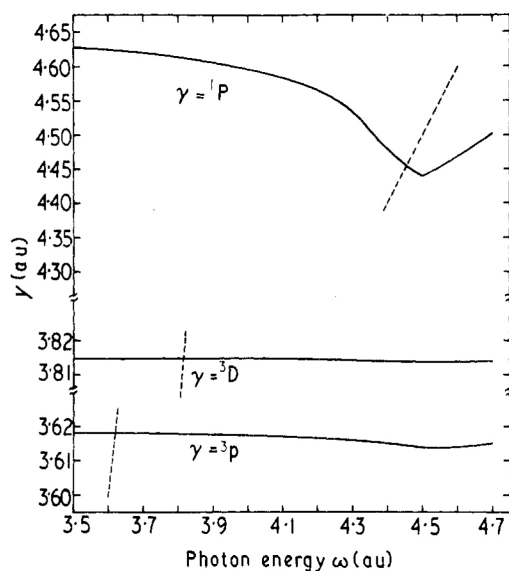


Figure 1. Plot of energy eigenvalues $y = E_\gamma(\omega)$ against photon energy ω for the three terms $\gamma = {}^1P, {}^3D, {}^3P$. Transition energies for each term γ are obtained as the energy ω at which the full curve $y = E_\gamma(\omega)$ and broken curve $y = \omega$ intersect, i.e., $E_\gamma(\omega) = \omega$.

Comparison with the experimental results of Zimkina *et al.* (1967) and Fomichev *et al.* (1967) is shown in Table 1. Also shown are the *ab initio* relative term energies computed by Dehmer and Starace (1972), which show clearly the usual problem in rare earth spectroscopy: calculated term separations are much larger than is experimentally observed. Our present results were calculated in much the same way except for our use of the effective electrostatic particle-hole interaction $\mathcal{V}^{LS}(\omega)$, which includes virtual 4d-shell excitations. Good agreement with experiment is obtained, although both our absolute and relative energies are still a few eV too high.

In Table 1 we have also included the results of Hansen (1972), who has calculated the $4d^9 4f$ term levels as the difference in total energy between the Hartree-Fock energies for the $4d^9 4f$ configuration and the $4d^{10}$ configuration of the triply-ionized La ion. Separate Hartree-Fock calculations were performed for *each term* of the $4d^9 4f$ configuration. A main result is that the $4f$ wavefunction for the 1P term extends out much further in coordinate space than either the $4f$ wavefunction resulting from an

Table 1. Comparison of calculated transition energies with experiment of Zimkina *et al.* (1967) and Fomichev *et al.* (1967). (All energies in eV; energy separation in parenthesis.)

Term	Experimental Energy	Dehmer and Starace (1972)*	Present Results	Hansen (1972)
1P	117 (15.4)	131.4 (28.7)	121.2 (17.4)	123.8 (21.0)
3D	101.6 (4.7)	102.7 (5.8)	103.8 (5.4)	102.8 (5.0)
3P	96.9	96.9	98.4	97.8

* Only relative energies calculated; absolute energies obtained by setting 3P energy equal to experiment.

Table 2. Analysis of effective electrostatic interaction. (All energies in atomic units: 1 au = 27.21 eV)

Term $F_{4f,4f}^{LS}(\omega)$	ω	$U_{4f,4f}^{LS}$	$\mathcal{V}_{4f,4f}^{LS}(\omega) - U_{4f,4f}^{LS}$	$F_{4f,4f}^{LS}(\omega)$	$\mathcal{V}_{4f,4f}^{LS}(\omega) +$
1P	4.4557	1.051	-0.129	-0.271	0.651
3D	3.8146	0.017	-0.0008	-0.00005	0.016
3P	3.6178	-0.147	-0.002	-0.002	-0.151

ordinary (term-independent) Hartree-Fock calculation or the Herman-Skillman 4f wavefunction employed here. As a result, the simplifying assumptions of Dehmer *et al.* (1971) arising from the nearly perfect overlap of the 4d and 4f wavefunctions do not obviously apply to a perturbation calculation based on Hansen's wavefunctions. Nevertheless, Hansen achieves a large reduction in the term splittings of the $4d^9 4f$ configuration as compared to Dehmer and Starace (1972). His calculation implicitly includes core relaxation effects, which are not considered here, but neglects virtual 4d-shell excitations that are considered here. Also, Hansen assumes $4d^9 4f$ to be a true bound state rather than an autoionizing resonance (as in this paper). Virtual 4d-shell excitations would be important in explaining the remaining discrepancy between Hansen's results and experiment, although they would not have the same magnitude as in this paper because of his different basis set. On the other hand, core relaxation is one of a number of processes not considered here that might explain the remaining discrepancies between our results and experiment.

The major *physical* difference between our present calculation and that of Dehmer and Starace (1972) is our inclusion of virtual 4d-shell excitations. One of the numerical differences that this leads to deserves mention. In Figure 1, the 1P eigenvalue curve $E_\gamma(\omega)$ has a dip near $\omega = 4.5$ au. This dip is caused by $F_{4f,4f}^{LS}(\omega)$, which has a minimum at this energy. Note that the dip causes the point of intersection, $E_\gamma(\omega) = \omega$, to occur at a lower photon energy than if there were no dip. In the calculation of Dehmer and Starace (1972), $F_{4f,4f}^{LS}(\omega)$ reaches its minimum value at a much lower photon energy and subsequently it rises sharply, causing the point of intersection to occur at much higher energies. The reason for the different behavior of $F_{4f,4f}^{LS}(\omega)$ that we observe is caused by our use of $\mathcal{V}^{LS}(\omega)$ in equation (14) rather than the approximate electrostatic interaction of Dehmer and Starace (1972).

In Table 2 we analyze the various contributions to the effective electrostatic interaction at the appropriate transition energies. We see that the total effective electrostatic interaction, $\mathcal{V}_{4f,4f}^{LS}(\omega) + F_{4f,4f}^{LS}(\omega)$ is 38% lower than for the 1P term and very little changed for the other terms. This comes about because only for the 1P term do both U^{LS} and \bar{U}^{LS} have a large contribution from the Slater exchange integral G^1 . Thus only for 1P are both real and virtual particle-hole interactions very large. This suggests that perhaps even in complex rare earth configurations only 4d-*cf* particle-hole pairs *that are coupled to* 1P need be considered when computing the effects of virtual 4d-shell excitations.

Conclusions

We have addressed ourselves in this paper to examining the causes of the well-known problem in theoretical rare earth spectroscopy that calculated term levels are much more widely separated than is observed experimentally. Dehmer and Starace (1972) avoided this problem in a study of the La IV $4d^9 4f$ configuration term levels, and one reason for choosing to study this configuration here is to extend this work.

Another reason is that the simple configuration $4d^9 4f$ is ideally suited for use of the random phase approximation to compute an effective interaction that includes virtual 4d-shell excitations. The absolute transition energies that we have calculated give quite good agreement with experiment. Furthermore, we have stressed in the Introduction that this calculation is not an isolated one. We expect that, in general, interactions between 4f-electrons in the rare earths are strongly modified (*i.e.*, reduced) by interaction with virtual 4d-shell excitations. From Table 2 it appears likely that only 4d-4f or 4d-ef particle-hole pairs that are coupled to 1P need be considered. Last, because of the potential barrier in the rare earths that produces very strong overlap of the 4d and 4f wavefunctions (Dehmer *et al.* 1971), we feel that methods such as those used in nuclear physics, of which the RPA is one, should be used to include virtual 4d-shell excitations to all orders.

References

- Altick, P. L., and Glassgold, A. E. 1964 *Phys. Rev.* **133** A632-46
- Amusia, M. Ya. 1971 in *Atomic Physics 2: Proceedings of the Second International Conference on Atomic Physics, July 21-24, 1970, Oxford*, ed. P. G. H. Sandars (London: Plenum), pp. 249-69
- Amusia, M. Ya., Cherepkov, N. A., and Chernysheva, L. V. 1971 *Zh. Eksp. Teor. Fiz.* **60** 160-74 [*Sov. Phys.-JETP* **33** 90-96]
- Brandow, B. H. 1967 *Rev. Mod. Phys.* **39** 771-828
- Brown, G. E. 1971 *Unified Theory of Nuclear Models and Forces*. 3rd ed (Amsterdam: North Holland), Chapter V
- Condon, E. U., and Shortley, G. H. 1935 *The Theory of Atomic Spectra* (London: Cambridge University Press), Chapter VII
- Dehmer, J. L., Starace, A. F., Fano, U., Sugar, J., and Cooper, J. W. 1971 *Phys. Rev. Lett.* **26** 1521-5
- Dehmer, J. L., and Starace, A. F. 1972 *Phys. Rev. B* **5** 1792-6
- Fano, U. 1961 *Phys. Rev.* **124** 1866-78
- Fano, U., and Cooper, J. W. 1968 *Rev. Mod. Phys.* **40** 441-507 § 8.5
- Feshbach, H. 1958 *Ann. Phys.* **5** 357-90
- Fetter, A. L., and Walecka, J. D. 1971 *Quantum Theory of Many-Particle Systems* (London: McGraw-Hill), Chapter 15
- Fomichev, V. A., Zimkina, T. M., Gribovskii, S. A., Zhukova, I. I. 1967 *Fiz. Tverd. Tela* **9** 1490-92 [*Sov. Phys.-Solid St.* **9** 1163-5]
- Gudat, W., and Kunz, C. 1972 *Phys. Rev. Lett.* **29** 169-72
- Haensel, R., Rabe, P., Sonntag, B. 1970 *Solid State Communications* **8** 1845-8
- Hansen, J. E. 1972 *J. Phys. B: Atom. Molec. Phys.* **5** 1096-1100
- Herman, F., and Skillman, S. 1963 *Atomic Structure Calculations* (Englewood Cliffs, New Jersey: Prentice-Hall)
- Kuo, T. T. S., and Brown, G. E. 1966 *Nucl Phys.* **85** 40-86
- Löwdin, P.-O. 1962 *J. Math. Phys.* **3** 969-82
- Morrison, J. C., and Rajnak, K. 1971 *Phys. Rev. A* **4** 536-42
- Newman, D. J., and Taylor, C. D. 1971 *J. Phys. B: Atom. Molec. Phys.* **4** 241-7
- Rowe, D. J. 1968 *Rev. Mod. Phys.* **40** 153-66
- Starace, A. F. 1972 *Phys. Rev. B* **5** 1773-84
- Sonntag, B., and Haensel, R. 1969 *Solid St. Commun.* **7** 597-9
- Sugar, J. 1972 *Phys. Rev. B* **5** 1785-92
- Trebbia, P., and Colliex, C. 1973 *Phys. Stat. Solidi (b)* **58** 523-32
- Wendin, G. 1971 *J. Phys. B: Atom. Molec. Phys.* **4** 1080-95
- . 1972 *J. Phys. B: Atom. Molec. Phys.* **5** 110-32
- . 1973 *J. Phys. B: Atom. Molec. Phys.* **6** 42-61
- Wybourne, B. G. 1965 *Spectroscopic Properties of Rare Earths* (New York: Interscience), §§ 2-18
- Zimkina, T. M., Fomichev, V. A., Gribovskii, S. A., Zhukova, I. I. 1967 *Fiz. Tverd. Tela* **9** 1447-50 [*Sov. Phys.-Solid St.* **9** 1128-30]
- Zimkina, T. M., and Gribovskii, S. A. 1971 *J. Phys. Paris* **32** Colloque C4 282-9