

# Two-electron-jump electric dipole oscillator strengths in $\text{La}^{48+}$ and $\text{La}^{49+}$

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We report nonrelativistic many-body  $f$  values for the La transitions  $2s2p^n \rightarrow 2s^22p^{n-2}3p$ , where  $n = 5, 6$ . The largest of these transitions, computed using the first-order theory of oscillator strengths and including all nonorthonormality effects, is about 0.009.

## I. INTRODUCTION

Recently Chandler, Chen, and Dietrich<sup>1</sup> have observed for the first time two-electron-jump transitions in a highly ionized atomic species. Specifically, they identify their observations as belonging to the  $2s2p^6 \rightarrow 2s^22p^43p$  transitions in  $\text{La}^{48+}$  and to the  $2s2p^5 \rightarrow 2s^22p^33p$  transitions in  $\text{La}^{49+}$ . Observations were made of the wavelengths only, which when compared with multiconfigurational Dirac-Fock (MCDF) calculations, showed constant deviations from the measured values.<sup>1</sup>

While transitions of such large  $Z$  ultimately deserve a full relativistic treatment, the method of doing so is just being completed;<sup>2</sup> moreover, for most of the transitions listed above, the MCDF procedure<sup>3</sup> must be generalized to permit inclusion of two (or more) configurations connected by a single excitation of the same symmetry. This situation has been discussed nonrelativistically by Froese-Fisher.<sup>4</sup> For these reasons, and because no results for the  $f$  values are available at all, we chose to explore these transitions from a nonrelativistic viewpoint.

## II. METHOD

The wave functions are obtained by using a perturbation-directed variational configuration-inter-

action (CI) method as described in Ref. 5. A zeroth-order wave function  $\Phi$  is first obtained from restricted Hartree-Fock (RHF) or multiconfigurational Hartree-Fock (MCHF) calculations using the program of Froese Fisher.<sup>6</sup> For this application, all  $2s2p^n$  zeroth-order wave functions were of the RHF type and, by necessity,<sup>4</sup> all  $2p^n3p$  terms which could be deexcited to the same  $2p^{n-1}$  term were of the MCDF type ( ${}^2P$  for  $n=4$  and  ${}^1S$ ,  ${}^3P$ ,  ${}^1D$  for  $n=3$ ) which contained  $2p^n3p$  and  $2p^{n-1}$  configurations. Although there is ample evidence (e.g., Ref. 4) that it is "unsafe" to use RHF results for cases such as this, we also did make RHF calculations for the  $2s^22p^43p$   ${}^2P$  term which yielded zeroth-order results little changed from the MCDF ones (in all cases we optimized the lowest  $2s^22p^n3p$  root). This may be of some use, should it not prove "simple" to modify the relativistic zeroth-order program<sup>3</sup> as described above.

Many-body effects are introduced by using perturbation theory to select the configurations to be added to those appearing in the zeroth-order function. If one uses first-order perturbation theory, as we do here, then all configurations must appear which are related by single and double subshell excitation to at least one configuration appearing in the zeroth-order function. Such configurations will introduce new (or "virtual") subshells, not present in  $\Phi$ . As is usual,<sup>5</sup> we will take a virtual spin-orbital to be the product of a spherical harmonic,

TABLE I. Application of FOTOS to the  $2s2p^6 \rightarrow 2s^22p^43p$  transition (neglecting nonorthonormality effects). The asterisk represents triple excitation from the zeroth-order configuration (triply excited configurations are not included in the calculation).

Initial configuration	Pseudoconfiguration	Pseudoconfiguration: result of applying $\hat{r}$	Final configurations
$2s2p^6$	$sp^6$	$p^7$	$2p^6(3p + vp^*)$
$2s2p^6$	$sp^6$	$s^2p^5$	$2s2p^5(2s + 3s + vs)$
$2s2p^6$	$sp^6$	$sp^5d$	$2s2p^5(3d + vd)$
$2s^22p^43p$	$s^2p^5$	$sp^6$	$2s2p^53p + 2s2p^43p^2 + 2s2p^43pvp$
$2s^22p^43p$	$s^2p^5$	$s^3p^4$	$2s^22p^33p(3s + vs)^* + 2s^22p^4(3s + vs)$
$2s^22p^43p$	$s^2p^5$	$s^2p^4d$	$2s^22p^4(3d + vd) + 2s^22p^33p(3d + vd)^*$

a spin function, and (prior to orthogonalization), a single Slater-type orbital (STO) whose exponent is determined by application of the energy variational principle to the configuration-interaction matrix.

Because the many-body function described above can be a fairly extensive one (hundreds of configurations), one seeks ways "tailored" to individual properties (e.g.,  $f$  values) to limit its size. One obvious choice is to exclude excitations from the 1s electrons (i.e., define them to form an "inactive" core), but this still leaves a fairly large function. To complement this, we use the first-order theory of oscillator strengths (FOTOS) which<sup>7</sup> identifies the crucial configurations needed in each state. This involves reduction of each zeroth-order configuration to a pseudoconfiguration (i.e., an entity which ignores the principal quantum number  $n$ ), application of the angular part of the transition operator,  $\hat{\tau}$ , to generate the pseudoconfigurations needed for the other state, and then conversion of these back to "actual" configurations (allowing for different levels of orthonormality). We illustrate the process in Table I for the  $2s2p^6 \rightarrow 2s^22p^43p$  transition, assuming full orthonormality. These configurations then become the crucial ones, but we must also include all other first-order configurations which significantly influence the virtual radial functions or coefficients associated with the FOTOS configuration. Past work (see, e.g., Ref. 5) suggests that the bivirtual parts of symmetry-adapted pair functions are nearly independent, so what we have chosen to do is to include the principal internal<sup>5</sup> effects (i.e., those which preserve the "complex"<sup>8</sup> along with the full bivirtual part of the  $2p^2$  pair (lower states) and the  $2s3p$  pair (upper state). It is of some interest, perhaps, to contrast this process to that used in the random-phase approximation (RPA)—firstly FOTOS excitations are made from both states, not just the ground states. Secondly, additional configurations which significantly influence the characteristics of the FOTOS configurations are included. Thirdly, both configurational coefficients and radial functions are optimized using the energy variational principle. It may also be noted that the procedure is more flexible in that any kind of state may be treated (not just closed shells), at any level (e.g., one may use a first-order function as a reference function), and that nonorthonormality effects may be treated exactly, partially, or neglected.

In Table II, we report our results for all transitions connecting  $2s2p^n$  and  $2s^22p^{n-2}3p$ . We can see that the zeroth-order (RHF) values are either zero (when there is no energetically lower configuration  $2s^22p^{(n-1)}$  associated with the upper state), or (when there is an energetically lower configuration) quite small, with vastly differing length and velocity values (arising from nonorthonormality effects). Thus (see also Ref. 9) double-jump transitions need not be identically zero at the zeroth-order level; nonorthogonality effects may yield a small, nonzero contribution. Once correlation effects are included, as described above, length and velocity results are brought into good agreement, although all transitions remain relatively weak (the largest is about 0.009, or more than ten times smaller than the usual allowed transition). We have also included the parental composition of the princi-

TABLE II.  $f$  values for  $2s2p^n \rightarrow 2s^22p^{n-2}3p$  La<sup>m+</sup> transitions. Values for length and velocity are calculated using RHF (first) and CI (second). Numbers in square brackets are exponents.

$\Delta E$ , <sup>a</sup> upper state (parental composition in parentheses <sup>b</sup> )	Length	Velocity
I. $n = 6, m = 48$	$^2S \rightarrow ^2P$	
175.695 (51.2, 44.9, 2.3)	0.158[-3] 0.124[-3]	0.469[-6] 0.142[-3]
177.880 (22.5, 40.7, 35.7)	0.887[-4] 0.892[-2]	0.257[-6] 0.875[-2]
178.241 (25.8, 12.1, 59.2)	0.178[-4] 0.312[-3]	0.513[-7] 0.262[-3]
II. $n = 5, m = 49$	$^3P^* \rightarrow ^3S$	
183.092 (0, 0, 96.4)	0.0 0.819[-3]	0.0 0.917[-3]
III. $n = 5, m = 49$	$^3P^* \rightarrow ^3P$	
181.209 (81.1, 14.8, 3.0)	0.785[-4] 0.987[-6]	0.186[-6] 0.657[-6]
183.428 (11.1, 78.6, 8.5)	0.993[-4] 0.438[-2]	0.230[-6] 0.448[-2]
183.794 (7.3, 3.0, 83.7)	0.597[-4] 0.167[-2]	0.138[-6] 0.158[-2]
IV. $n = 5, m = 49$	$^3P^* \rightarrow ^3D$	
182.271 (0, 92.5, 5.7)	0.0 0.426[-4]	0.0 0.493[-4]
183.345 (0, 6.1, 92.0)	0.0 0.182[-2]	0.0 0.207[-2]
V. $n = 5, m = 49$	$^1P^* \rightarrow ^1S$	
182.247 (0, 0, 98.1)	0.320[-5] 0.188[-2]	0.688[-8] 0.194[-2]
VI. $n = 5, m = 49$	$^1P^* \rightarrow ^1P$	
178.964 (0, 81.4, 16.7)	0.0 0.177[-4]	0.0 0.261[-4]
180.408 (0, 0, 17.4, 81.1)	0.0 0.989[-3]	0.0 0.112[-2]
VII. $n = 5, m = 49$	$^1P^* \rightarrow ^1D$	
180.393 (0, 40.3, 58.4)	0.861[-4] 0.216[-2]	0.189[-6] 0.229[-2]
181.301 (0, 59.2, 39.2)	0.260[-3] 0.675[-3]	0.564[-6] 0.539[-3]

<sup>a</sup>CI excitation energy in a.u.

<sup>b</sup>% composition of  $^3P$ ,  $^1D$ ,  $^1S$  parents of  $2s^22p^43p$  for  $n = 6$  and of  $^4S$ ,  $^2D$ ,  $^2P^*$  parents of  $2s^22p^33p$  for  $n = 5$  in the CI wave function, respectively. When more than one upper state of a given  $L$  and  $S$  is possible, multiple entries are given, once for each upper state.

pal configuration for the excited state in Table II.

Usually, we prefer to use the experimental excitation energy when reporting  $f$  values; this is consistent with FOTOS, whose primary focus is on the transition matrix element. Here, we have not done this, because such energies, even if available, may well contain substantial relativistic effects, and our calculations are nonrelativistic ones. But since we have truncated (via FOTOS) the "complete" first-order energy calculation, we must determine the error introduced in the excitation energy. But nonrelativistic correlation energy is a few a.u. at best; if one examines the excitation energies of Table II, one can see that all of them are around 180 a.u. Therefore we estimate that less than a 1% error will be introduced in the excitation energy by our truncations. To investigate this, we recalculated the  $2s2p^5\ ^3P \rightarrow 2s^22p^33p\ ^3S$  excitation energy using a full (core = 1s) first-order function. The excitation energy was lowered by 0.05%, an entirely acceptable error in the present context. We should also note that the size of the calculation increased from an energy matrix of order 36 to one of order 180 with the inclusion

of these effects.

It is also of interest to compare the role of nonrelativistic correlation effects in higher- $Z$  species to that played for small- $Z$  species; while for both, the effect on the energy can be large (several eV or more), for the higher- $Z$  species many configurational coefficients become much smaller, indicating that for properties other than energy, such configurations may well play much smaller roles. In terms of first-order perturbation theory, this arises from very large energy denominators and energy numerators (off-diagonal matrix elements) which are greater than 1.0 in magnitude. Physically, of course, it is associated with approach to the hydrogenic limit, which gives a relatively greater role to the "complex."

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<sup>1</sup>G. A. Chandler, M. H. Chen, and D. D. Dietrich, Bull. Am. Phys. Soc. **33**, 946 (1988).

<sup>2</sup>D. R. Beck and Z. Cai (unpublished).

<sup>3</sup>J. P. Desclaux, Comput. Phys. Comm. **9**, 31 (1975).

<sup>4</sup>C. Froese Fisher, Phys. Rev. Lett. **38**, 1075 (1977).

<sup>5</sup>D. R. Beck and C. A. Nicolaides, in *Excited States in Quantum Chemistry*, edited by C. A. Nicolaides and D. R. Beck (Reidel, Dordrecht, 1978), pp. 105 ff.

<sup>6</sup>C. Froese Fisher, Comput. Phys. Comm. **4**, 107 (1972).

<sup>7</sup>C. A. Nicolaides and D. R. Beck, Chem. Phys. Lett. **36**, 79 (1975).

<sup>8</sup>D. Layzer, Z. Horak, M. Lewis, and D. Thompson, Ann. Phys. (N.Y.) **29**, 101 (1964).

<sup>9</sup>C. A. Nicolaides and D. R. Beck, J. Chem. Phys. **66**, 1982 (1977).