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Calculations of oscillator strengths and excitation energies for valence-shell states of Mg and Ca†

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Oscillator strengths and excitation energies are computed for electric dipole transitions connecting valence-shell states of Mg I and of Ca I. The method used is the variational solution of two-particle Bethe-Goldstone equations for both initial and final states of each transition, with a common frozen core determined by a matrix Hartree-Fock calculation. Results are compared with available theoretical and experimental data, and are found to be in excellent agreement with previous results for the two resonance transitions. For Mg, the computed length and velocity oscillator strengths are closer together for most transitions considered than are previous theoretical values, and fall within their range. For Ca, the computed results confirm conclusions about valence-shell even-parity states inferred from analysis of recently observed two-photon ionization spectra.

I. INTRODUCTION

Rydberg series of even-parity $J=0$ and 2 states in Ca have recently been observed by two-photon laser spectroscopy.[1] The observed energy levels were analyzed by multichannel quantum-defect theory.[2,3] This theory makes use of the asymptotic behavior of Coulomb wave functions. Hence it is valid for orbital wave functions outside the valence shell, but must be augmented by a more detailed description of states involving valence shell orbitals. As a preliminary step toward a fully quantitative theory, including two-photon intensities, the present paper reports results of calculations of energy levels for valence shell excited states of Mg and Ca and of oscillator strengths for electric dipole-allowed transitions among these states.

There have been many previous theoretical studies of the resonance transitions $(3s^2)\,^1S \rightarrow (3s3p)\,^1P^o$ in Mg (Refs. 4–9) and $(4s^2)\,^1S \rightarrow (4s4p)\,^1P^o$ in Ca.[10-12] Reference is given here to the most recent calculations. Transitions to even-parity states from the $(nsnp)\,^{1,3}P^o$ states have been less thoroughly studied. The most complete survey is that of Victor *et al.*[4,10] who used a semiempirical two-electron model potential.[13] The present calculations treat all orbital functions explicitly, without semiempirical parametrization.

Details of the computations are given in Sec. II and results are presented in Sec. III.

II. COMPUTATIONAL METHOD

The present work uses the same method as previously applied[14] to valence shell excitations Be, except that inner shell virtual excitations are not considered here. The theoretical model uses valence shell configuration $nsnp$ as reference ($3s3p$ for Mg; $4s4p$ for Ca) and considers all virtual excitations at level $[nsnp]_2$, in the notation defined previously.[14] This is a frozen-core approximation, with variational solution for the two outer electrons, limited only by the orbital basis set used. For singlet states, reference orbitals are determined by a preliminary matrix Hartree-Fock calculation on state $(nsnp)\,^1P^o$, and for triplet states, by a similar calculation on state $(nsnp)\,^3P^o$.

The orbital basis sets used are defined in Table I. All configurations of structure $[nsnp]_2$ in the linear space generated by these basis orbitals were included in the variational calculations. The basis sets shown are obtained by augmenting ground-state double-zeta functions[15] by additional orbitals whose exponents form a geometric series. An extensive series of preliminary calculations was carried out on the Mg and Ca resonance transitions to examine the effects of variations of the basis sets. The criterion used was stationarity of the computed excitation energy. This criterion is not rigorous,

TABLE I. Parameters ζ for basis orbitals $r^{n-1} \times \exp(-\zeta r)$, in addition to double zeta (Clementi and Roetti, Ref. 15) for inner shells.

Mg(7, 5, 4, 1)		Ca(9, 7, 5)	
$3s$	1.47233	$4s$	1.43414
	0.89173		0.86666
	0.54008		0.52373
$3p$	1.47233	$4p$	1.43414
	0.89173		0.86666
	0.54008		0.52373
$3d$	1.47233	$3d$	3.92715
	0.89173		2.37320
	0.54008		1.43414
	0.32711		0.86666
			0.52373
$4f$	0.89173		

but would apply to exact wave functions. The preliminary investigation indicated that the very simply defined basis sets of Table I could not be substantially improved without adding orbitals of higher l values or relaxing the frozen-core approximation.

The notation Mg(7, 5, 4, 1) in Table I indicates that the orbital basis for Mg includes 7, 5, 4, and 1 independent radial functions of type s, p, d, and f, respectively. Similarly, Ca(9, 7, 5) indicates 9, 7, and 5 functions of type s, p, d, respectively.

A $3d$ orbital is defined by a matrix Hartree-Fock calculation on the state $(ns3d)\,^3D$, with $n=3$ for Mg and $n=4$ for Ca. A specified state of configuration $3d^2$ is identified by scanning eigenvectors of the configuration interaction matrix for the one with greatest weight in the designated configuration.[16] The N-electron wave functions are independent of this arbitrary definition of the $3d$ orbital since they include all basis d orbitals equivalently. The $^{1,3}D$ states of configuration $3s3d$ for Mg or $4s3d$ for Ca are uniquely defined as the lowest states of their symmetry type. In each case it is found that the nominal configuration $3s3d$ or $4s3d$, respectively, corresponds to the dominant eigenvector component.

III. RESULTS

Results for Mg are shown in Table II, and compared with recent theoretical[4-9] and experimental[17-20] data. Experimental energy levels are from Risberg[21] or Moore.[22] The general agreement with previous results is good.

The most complete theoretical calculations for Mg are those of Weiss,[5] who used a (7, 3) orbital basis set for the ground state, augmented by additional orbitals for excited states, included configuration interaction for the two valence electrons, as in the present work, but carried out separate matrix Hartree-Fock calculations for each state considered. To test the possible significance of this latter point, both $(3s3p)\,^3P^o$ and $(3s3d)\,^3D$ were used as reference states (defined by matrix Hartree-Fock calculations) to compute the transition energy and oscillator strength between these two states. For Mg, the difference in results was negligible, not affecting the numbers shown in Table II. A similar comparison for Ca shows a much larger effect, which can be attributed in that case to perturbation of the $3s^23p^6$ core by the $3d$ orbital.

TABLE II. Mg excitation energies (Hartree atomic units) and oscillator strengths.

State Initial	State Final	ΔE(obs)[a] (cm^{-1})	ΔE(obs)[a] (a.u.)	ΔE(calc) (a.u.)	f(calc) f_l	f(calc) f_v	f (other)
$3s^2\ ^1S$	$3s3p\ ^1P^o$	35051	0.15971	0.15673	1.746	1.717	1.72,[b] 1.737,[c] 1.665,[d] 1.757,[e] 1.760,[f] 1.86,[g] 2.4,[h] 1.75[i]
	$3s$ limit	61671	0.28100				
$3s3p\ ^1P^o$	$3s3d\ ^1D$	11352	0.05172	0.04836	0.205	0.198	0.290,[b] 0.232[c]
	$3s$ limit	26620	0.12129				
	$3p^2\ ^1S$			0.14685	0.201	0.196	
	$3p^2\ ^1D$			0.21923	0.096	0.115	
	$3p$ limit	62350	0.28409				
	$3d^2\ ^1D$			0.35688	0.003	0.006	
	$3d^2\ ^1S$			0.37046	0.000	0.000	
	$3d$ limit	98111	0.44703				
$3s3p\ ^3P^o$	$3s3d\ ^3D$	26066	0.11877	0.11936	0.655	0.634	0.618,[b] 0.570,[c] 0.565,[i] 0.56,[j]
	$3p^2\ ^3P$	35963	0.16386	0.16043	0.640	0.630	0.607,[b] 0.635,[c] 0.621,[k] 0.50,[h] 0.552[i]
	$3s$ limit	39780	0.18125				
	$3p$ limit	75510	0.34405				
	$3d^2\ ^3P$			0.42180	0.000	0.000	
	$3d$ limit	111271	0.50699				

[a] Risberg, Ref. 21, or Moore, Ref. 22.
[b] Victor *et al.*, Ref. 4.
[c] Weiss, Ref. 5.
[d] Stewart, Ref. 6.
[e] Fischer, Ref. 7.
[f] Saraph, Ref. 9.
[g] Smith and Lizst, Ref. 17.
[h] Berry *et al.*, Ref. 18.
[i] Lundin *et al.*, Ref. 19.
[j] Andersèn *et al.*, Ref. 20.
[k] Beck and Sinanoğlu, Ref. 8.

The present f_l and f_v values are generally closer together than those of Weiss,[5] indicating somewhat better convergence of the present calculations. For the resonance transition, Weiss has $f_l = 1.773$, $f_v = 1.701$; for $(3s3p)\,^1P^o \rightarrow (3s3d)\,^1D$, $f_l = 0.279$, $f_v = 0.185$; and for $(3s3p)\,^3P^o \rightarrow (3p^2)\,^3P$, $f_l = 0.654$, $f_v = 0.615$. The present values, shown in Table II, are closer together and fall in between the f_l and f_v values of Weiss. The only apparent discrepancy is for the $(3s3p)\,^3P^o \rightarrow (3s3d)\,^3D$ transition, where Weiss has $f_l = 0.572$, $f_v = 0.569$, outside the range of the present values and closer together. His computed energy is 0.1193 a.u. exactly equal to the present value. The experimental results appear to favor the lower value of f in this case. A careful study of convergence for this particular transition and examination of inner shell effects would be needed before a definitive choice could be made among the available results.

The states of configuration $3p^2$ and $3d^2$ lie above the $3s$ or $3p$ ionization limits and correspond to autoionizing states. The lifetime or width depends on the strength of interaction with the ionization continuum. The computed energies should lie within the width of these resonances.[16] In the particular case of the state labeled $(3p^2)\,^1D$, the $3p^2$ configuration is also a large component of the wave function computed at $\Delta E = 0.13491$ a.u., below the $(3p^2)\,^1S$ state. This may indicate a very broad resonance, or sharing of oscillator strength from $3p^2$ over a broad range of ^1D states, including the continuum extending beyond the $3snd$ Rydberg-series limit.

Results for Ca are shown in Table III, compared with theoretical [10–12] and experimental[17] data. Experimental energy levels are from Risberg[23] or Moore.[22] Agreement with previous results for the resonance transition and for the transition $(4s4p)\,^3P^o \rightarrow (4p^2)\,^3P$ is good. For the transition $(4s4p)\,^1P^o \rightarrow (4p^2)\,^1D$ the present values of the oscillator strength are an order of magnitude larger than an earlier calculation,[11] which, however, used much more restricted variational wave functions.

Configurations $4s3d$, $4p^2$, and $3d^2$ are found to interact strongly in the ^1D states. While configurations $4s3d$ and $3d^2$ are the largest single components of the ^1D states so labeled, the state designated $(4p^2)\,^1D$ has nearly equal weights from all three. This may account for the very large oscillator strength computed for the transition from $(4s4p)\,^1P^o$ to this state.

The ^1D and ^1S states identified with configuration $3d^2$ are computed to be above the $4s$ ionization limit, in agreement with conclusions by Armstrong *et al.*,[1] from multichannel quantum defect analysis of their data. They reassign the state designated $(3d^2)^1D$ by Risberg[23] to $(3d5s)\,^1D$, and find no ^1D state below the $4s$ limit that can be labeled $3d^2$, although the $4snd$ Rydberg series shows an admixture attributed to this configuration. This is in accord with the present calculation of a substantial oscillator strength in the $(4s4p)\,^1P^o \rightarrow (3d^2)\,^1D$ transition, and strong configuration mixing involving $(3d^2)\,^1D$. This state would be characterized as a broad resonance in the $4snd$ ionization continuum,

TABLE III. Ca excitation energies (Hartree units) and oscillator strengths.

State Initial	 Final	ΔE(obs) [a] (cm^{-1})	 (a.u.)	ΔE(calc) (a.u.)	f (calc) f_l	 f_v	 f (other)
$4s^2\ ^1S$	$4s4p\ ^1P^o$	23652	0.10777	0.10419	1.885	1.782	1.822,[b] 1.75,[c] 1.83,[d] 1.75[e]
	$4s$ limit	49306	0.22465				
	$3d$ limit	62992	0.28702				
$4s4p\ ^1P^o$	$4s3d\ ^1D$	−1803	−0.00821	0.00650	0.001	0.013	
	$4p^2\ ^1D$	17068	0.07777	0.09025	1.694	1.380	0.17[c]
	$4p^2\ ^1S$	18134	0.08263	0.08297	0.157	0.197	
	$4s$ limit	25653	0.11689				
	$3d^2\ ^1D$	f		0.14155	0.326	0.181	
	$3d^2\ ^1S$			0.16495	0.010	0.006	
	$3d$ limit	39340	0.17925				
$4s4p\ ^3P^o$	$4s3d\ ^3D$	5094	0.02321	0.05013	0.255	0.259	
	$4p^2\ ^3P$	23245	0.10591	0.10469	0.622	0.623	0.514,[b] 0.52[c]
	$3d^2\ ^3P$	33288	0.15167	0.17674	0.044	0.033	0.104[b]
	$4s$ limit	34043	0.15511				
	$3d$ limit	47729	0.21747				

[a] Risberg, Ref. 23, or Moore, Ref. 22.

[b] Victor *et al.*, Ref. 10.

[c] Friedrich and Trefftz, Ref. 11.

[d] Kim and Bagus, Ref. 12.

[e] Smith and Lizst, Ref. 17.

[f] The state classified as $(3d^2)\,^1D$ in Ref. 24 is reassigned to $(3d5s)\,^1D$ in Ref. 1, and $(3d^2)\,^1D$ is not identified below the $4s$ limit.

extending down into the Rydberg series.

The $4s^2$, $4p^2$, and $3d^2$ configurations are found to interact strongly in the computed ^1S states. Configuration $4s^2$ dominates the ground state, but $4p^2$ and $3d^2$ occur with nearly equal weight in the ^1S states so labeled. The lower of the two states is designated as $(4p^2)\,{}^1S$ in Table III. The computed excitation energy is in excellent agreement with the state denoted $(4p^2)\,{}^1S$ by Risberg.[23] The transition to the upper state, labeled $(3d^2)\,{}^1S$ in Table III, is found to have a smaller oscillator strength. This agrees with the finding by Armstrong *et al.*[1] that only two independent "unperturbed" series, states $4sns$ and the unique interloper state labeled $(4p^2)\,{}^1S$, need be considered in analysis of the observed ^1S Rydberg series. Nevertheless, the present calculations show that it cannot be concluded from such analysis that an isolated state belongs to a pure configuration.

Although configurations $4p^2$ and $3d^2$ also interact strongly in the computed ^3P states, one configuration clearly dominates each of the computed wave functions, so the designation of these states in Table III is unambiguous. The computed $(4s4p)\,{}^3P^o \rightarrow (4p^2)\,{}^3P$ transition energy is close to its spectroscopic value.[23] For both $(4s3d)\,{}^3D$ and $(3d^2)\,{}^3P$ the computed excitation energy is too high by approximately 0.025 a.u., probably indicating a quantitative inadequacy of the frozen core approximation for configurations involving $3d$ orbitals. Although the computed $(3d^2)\,{}^3P$ energy is above the $4s$ limit, the state is still bound, since autoionization into the $4snl$ continuum is parity forbidden.

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