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Calculations of the $2sns\ ^1S$ and $2p3p\ ^3,^1P$ Levels of Be I^\dagger

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Large scale configuration-interaction calculations are carried out on the $2sns\ ^1S$ series of Be I in an attempt to account for the anomalous behavior of the measured f value for the 3455-Å line, which had been identified as the $2s2p\ ^1P-2p^2\ ^1S$ transition. The calculations indicate that the series is very nearly purely Rydberg in character and that $2p^2\ ^1S$ is not embedded in the series between $6s$ and $7s$, as had been previously assigned. Additional variational calculations on the $2snp$ and $2p3p$ levels indicate that a reidentification of the 3455-Å line with the $2s3p\ ^1P-2p3p\ ^1P$ transition is consistent with both lifetime and wavelength measurements. These calculations also predict lines at 2148 and 4528 Å, which have recently been found in beam-foil spectra.

I. INTRODUCTION

Recent beam-foil lifetime measurements¹⁻³ have consistently given an f value for a transition classified as $2s2p\ ^1P-2p^2\ ^1S$ in Be I (3455 Å) which appears to be inconsistent with the established systematic trend for the isoelectronic sequence.⁴ Such systematic trends have, by now, been sufficiently well established⁵ that one can meaningfully search for a physical explanation for departures from the regular behavior. In this case the obvious first clue seems to be the fact that the $2p^2$ term is embedded in the $2sns\ ^1S$ series with the resulting series interaction presumably being responsible for the f -value anomaly. The problem is that a preliminary study shows the integrals coupling the perturber to the series are very small, indicating a very weak series perturbation effect. This is further supported by the experimental quantum defects which show essentially no effect of the series-perturber interaction.⁶

This paper reports a set of large scale configuration-interaction (CI) calculations on the 1S series to investigate quantitatively the structure of the series wave functions as well as to calculate the f values, and these calculations are reported and discussed in the Sec. II. Since the main interest is in the series as a whole, a common-orbital basis is used for all the states, necessitating the use of a somewhat larger CI than would be needed for any one state. As we will see, the calculations indicate that for $2s3s-2s7s$, the 1S states

are all Rydberg-like with only a very small admixture of $2p^2$. Since the original analysis of the spectrum places the perturber between $6s$ and $7s$,⁶ this suggests a misassignment of the $2p^2$ level, an assignment which was originally based on only the one line at 3455 Å.

Section III then describes a set of follow-up calculations designed to search for a plausible classification for the 3455-Å line. Variational superposition-of-configurations (SOC) calculations are reported for the 3P and, previously unknown, 1P terms of the $2p3p$ configuration. When combined with similar calculations on the $2snp$ ($n=2-4$) levels, the predicted wavelengths and lifetimes are consistent with the new experimental data⁷ and with an assignment of 3455 Å as the $2s3p\ ^1P-2p3p\ ^1P$ transition. This would place the $2p3p\ ^1P$ level at 89121 cm^{-1} above the ground state.

II. CONFIGURATION INTERACTION IN 1S SERIES

The wave functions for the 1S state are all CI-type functions,

$$\Psi = \sum_i a_i \phi_i, \quad (1)$$

where the ϕ_i are antisymmetrized products (properly \mathcal{L}^2 and S^2 projected) of one-electron functions, or orbitals. One of the crucial questions for such a multiconfiguration trial function always concerns the choice of the orbital set.⁴ On the one hand, one can use a set of spectroscopically realistic orbitals which give a reasonable zeroth-order ap-

proximation for the excited states. While this provides approximate wave functions for all the states in terms of a single set of configurations, there are often problems of slow convergence and the necessity of using continuum orbitals. On the other hand, one can treat each state individually using variationally optimum correlation orbitals to minimize the energy of the appropriate root of the matrix-eigenvalue equation. While this procedure, which is more appropriately labeled SOC, can give an accurate approximation for each state, it may tend to obscure the global picture of the spectrum which is so transparent in the other approach.

Since we are here interested in an accurate overview of the entire 1S spectrum, or at least the lowest six or seven members, a compromise combination of the two approaches is used here. A single set of orbitals including both Rydberg and correlation types is used in generating a common set of configurations for all the S states. Relaxation effects and differential correlation effects in the different states are allowed for simply by including a large number of configurations, some of which will be important for one state and not for another. Beryllium is a simple enough atom to make such a scheme feasible.

The orbitals are expressed as a linear combination of Slater-type basis functions,⁸

$$\chi_{ql}(\xi) = (2\xi)^{q+1/2} [(2q)!]^{-1/2} r^{q-1} e^{-\xi r} Y_l^m(\vartheta, \varphi). \quad (2)$$

For the p orbitals, the expansion method Hartree-Fock (HF) basis of the $2p^2 \ ^1S$ was used originally, with some later basis set augmentation. For the s orbitals, the HF basis for the $2s^2 \ ^1S$ ground state⁹ was used to begin with and was successively augmented for each excited state. This was done in the following way: For the first excited state a Slater-type $3s$ function was added to the ground-state basis, and the ζ varied to minimize the second eigenvalue of the CI function,

$$\Psi^{(1)} = \sum_{nn'} a_{nn'} (nsn's \ ^1S) + \sum_{mm'} b_{mm'} (mpm'p \ ^1S), \quad (3)$$

where the nl orbitals were obtained by successively orthogonalizing the full s and p basis to the HF orbitals and themselves. This was followed by a two-electron natural orbital transformation¹⁰ generating a $3s$ orbital which, while Rydberg-like, is not quite the HF $3s$, since the effect of $2p^2$ -type correlation was allowed for in the original trial function. This process was repeated for the next excited state adding a $4s$ function to the basis, then $5s$, etc., up through $7s$.

The next step was to generate a set of $n = 2$ shell correlation orbitals. This was done by sitting on the eigenvalue which was predominantly $2p^2$, adding more Slater-type basis functions—one $3s$, one

$3p$, three $3d$, and one $4f$ —and varying their ζ 's. A natural orbital transformation was then carried out to optimize the form of the correlation orbitals, the s functions then being orthogonalized to the Rydberg set. There is considerable relaxation in the $2s$ orbital from the ground state to the Rydbergs, and the $2s$ selected for the final wave function was taken from $2s5s$ as being more or less typical for a Rydberg state. The relaxation for the lower states was made up for by a number of the $2sns$ and $nsn's$ types of configurations.

The wave function finally settled on consisted of 39 configurations, and the results are summarized in Table I. Since the intention is to display the dominant structure of the 1S states, the complete wave functions are not given—only those configurations with a coefficient greater than 0.03 for any state are listed. The correlation s orbitals are labeled s_1 and s_2 . Aside from the $2s^2$ ground state, with its well-known strong admixture of $2p^2$, all the bound states turn out to be overwhelmingly $2sns$ for $n = 3-7$. This search thus fails to give a bound state which is predominantly $2p^2$, disagreeing with the experimental assignment of $2p^2 \ ^1S$ as lying between $6s$ and $7s$. Except for the ground state, the 1S series term positions are also calculated quite accurately for an *ab initio* calculation, with errors ranging from 60 to 95 cm^{-1} . Even for the ground state the results are quite good—a correlated SOC-type calculation¹¹ gives a total energy of -14.61886 compared to the present result -14.61842 , a difference of 0.01 eV. This seems to indicate that the orbital and configuration bases are adequate for representing the $n = 2$ shell correlation.

The $2p^2 \ ^1S$ level is here predicted to lie about 0.23 eV above the ionization limit, a prediction, however, which may not be quantitatively meaningful. The CI configuration basis was only carried through $2s7s$, and if the $2p^2$ were higher up in the discrete spectrum, say between $8s$ and $9s$, these calculations would not be properly designed to find it. The calculations do seem to indicate rather strongly that it is not between $6s$ and $7s$, meaning that the assignment of the 3455-Å line is incorrect. For what it may be worth, a sequence of CI calculations was also done, successively omitting the $2s7s$ Rydberg configuration, then the $6s$, etc., each time focusing on one lower root of the matrix eigenvalue equation. These results are summarized in Table II, which shows that the predicted position of $2p^2$ is essentially insensitive to the number of lower Rydberg terms in the wave function. While this would seem to suggest that including still more series members would not alter its predicted position as an autoionizing state, it must be emphasized that this is only conjecture.

Since the wave functions were on hand, the os-

TABLE I. The lowest energies and dominant configurations of the 39-configuration 1S wave functions for BeI. Total energies are in atomic units (1 a. u. = 219 461 cm^{-1}). Term energies are relative to the $2s^2S$ limit of the ion, with the theoretical values calculated relative to the HF limit of -14.277 40 a. u. The nominal designations of the states are given as the column headings.

State	$2s^2$	$2s3s$	$2s4s$	$2s5s$	$2s6s$	$2s7s$	$2p^2$
$-E_{\text{tot}}$ (a. u.)	14.618 42	14.370 51	14.322 29	14.303 88	14.294 73	14.289 53	14.269 14
Term energy (cm^{-1})							
Calc.	-74 841	-20 434	-9852	-5811	-3803	-2673	+1813
Expt. ^a	-75 192	-20 515	-9947	-5870	-3871	-2744	
Error	351	81	95	59	68	71	
Configurations and coefficients							
$2s^2$	0.933	-0.101	0.044	-0.010	0.011	-0.007	0.239
$2s3s$	0.126	0.980	0.018	-0.011	0.008	-0.006	0.021
$2s4s$	-0.063	0.001	0.994	0.026	-0.005	0.002	0.008
$2s5s$	0.028	0.000	-0.019	0.996	0.039	0.002	-0.018
$2s6s$	-0.029	0.001	0.000	-0.034	0.996	0.043	0.019
$2s7s$	0.024	-0.001	0.003	-0.004	-0.039	0.997	-0.021
$2s5s_1$	-0.130	0.008	-0.009	0.014	-0.030	0.030	-0.069
$2s5s_2$	-0.001	-0.006	0.012	0.001	0.023	-0.022	0.031
$2p^2$	-0.273	0.031	-0.032	0.031	-0.031	0.029	0.926
$2p3p$	-0.115	0.150	-0.078	0.053	-0.039	0.030	-0.092
$3p^2$	-0.027	0.051	-0.025	0.015	-0.010	0.007	-0.186
$2p4p$	-0.023	0.035	0.004	-0.006	0.006	-0.005	-0.060
$3d^2$	-0.017	-0.012	0.010	-0.009	0.008	-0.007	-0.168

^aSee L. Johansson, Ref. 6.

cillator strengths were also computed for transitions to the $2snp$ ($n=2-4$) levels, and these results, along with the predicted lifetimes, are given in Table III. The lifetimes for the higher levels are only upper limits, since some of the higher np branchings are omitted. For instance, a Coulomb-approximation¹² estimate for $6s-5p$ ($\lambda=83\ 300$) gave an A value of $1.1 \times 10^6 \text{ sec}^{-1}$, and lowered the length and velocity lifetimes to 125 and 127 nsec, respectively. The $2snp$ states were represented by variational SOC wave functions, which will be described in Sec. III.

The conclusions derived from these results thus appear to be the following: (i) The coupling between $2p^2\ ^1S$ and the s series is indeed very weak, in agreement with the experimental quantum defects. (ii) The $2p^2$ term is not found to lie between the $6s$

and $7s$ series members, in contradiction with the spectroscopic assignment. (iii) There is the strong suggestion that $2p^2$ should be an autoionizing state, and it is estimated to be about 0.23 eV above the limit.

III. SOC CALCULATION ON THE $2snp$ AND $2p3p$ LEVELS

If the second conclusion of Sec. II is correct, then it is necessary to search for a plausible alternative classification for the 3455 line. The most likely candidate would appear to be a transition involving the previously unassigned 1P term of $2p3p$. The 3P term is known and its location is such that the $2s3p-2p3p$ singlet transition might be in the neighborhood of 3455 Å. Although these levels lie above the ionization limit, as even-parity P states, they should have relatively long lifetimes

TABLE II. Total energies (in a. u.) and most important terms for a sequence of predominantly $2p^2$ wave functions generated by omitting successively more Rydberg configurations.

Function	$2s^2-2s7s$	$2s^2-2s6s$	$2s^2-2s5s$	$2s^2-2s4s$	$2s^2$
No. config.	39	38	37	36	34
Root	7th	6th	5th	4th	2nd
E_{tot}	-14.269 14	-14.269 14	-14.269 15	-14.269 17	-14.269 21
Configurations and coefficients					
$2s^2$	0.239	0.239	0.239	0.239	0.239
$2p^2$	0.926	0.926	0.927	0.927	0.926
$3p^2$	-0.186	-0.185	-0.185	-0.185	-0.186
$3d^2$	-0.168	-0.168	-0.168	-0.168	-0.168

TABLE III. Oscillator strengths, transition probabilities, and lifetimes for the 1S series through $7s$.

Transition	λ (Å)	f		A (10^8 sec^{-1})		τ (nsec)	
		len.	vel.	len.	vel.	len.	vel.
$2s2p^1P - 2s3s^1S$	8 256	0.127	0.121	0.373	0.355	26.8	28.2
$2s2p^1P - 2s4s^1S$	4 409	0.0091	0.0103	0.094	0.106		
$2s3p^1P - 2s4s^1S$	19 770	0.223	0.207	0.114	0.106	48.1	47.2
$2s2p^1P - 2s5s^1S$	3 737	0.0035	0.0039	0.050	0.056		
$2s3p^1P - 2s5s^1S$	10 950	0.057	0.022	0.095	0.037		
$2s4p^1P - 2s5s^1S$	43 730	0.310	0.306	0.032	0.032	56.5	80.0
$2s2p^1P - 2s6s^1S$	3 478	0.0020	0.0022	0.033	0.036		
$2s3p^1P - 2s6s^1S$	8 982	0.0088	0.0074	0.022	0.018		
$2s4p^1P - 2s6s^1S$	23 330	0.0383	0.0393	0.014	0.014	145	147
$2s2p^1P - 2s7s^1S$	3 346	0.0013	0.0014	0.023	0.025		
$2s3p^1P - 2s7s^1S$	8 156	0.0036	0.0037	0.011	0.011		
$2s4p^1P - 2s7s^1S$	18 470	0.0137	0.0141	0.008	0.008	238	227

inst autoionization.

Since the primary interest here is to obtain as accurate an approximation as possible for the wave function and energies, rather than to exhibit the structure of an entire series, each state was treated independently by separate SOC calculations. The procedure is the same as has been used extensively before for oscillator strengths and energies.¹³ Starting with an expansion method HF function, the basis set is augmented and the parameters varied to minimize the energy of the appropriate root for a large two-electron SOC trial function. This is followed by a pseudonatural orbital transformation^{13,14} to generate an optimum set of correlation orbitals which usually condenses the relevant correlation content of the wave function into relatively few configurations. For $2s3p$, $2s4p$, and $2p3p$, the occupied orbitals are not quite HF, since the first natural orbitals of the pseudonatural orbital transformation were used.

The results of the energy calculations are given in Table IV. The triplet system was also calculated, since $2p3p^3P$ is well known experimentally, and this data should provide an extra handle on assessing the accuracy of the singlet calculations. The 1P term of $2p3p$ is the lowest of its symmetry, while the 3P is the second lowest. The predicted-term energies are obtained by subtracting from the SOC total energy the HF total energy for the appropriate ionization limit, i. e., the $2s$ limit for the $2snp$ levels and the $2p$ limit for $2p3p$ and $2p3s$. The errors in the theoretical spectrum range from 550 cm^{-1} (for $2s2p^1P$) to 50 cm^{-1} , which is certainly satisfactory for *ab initio* calculations, although, curiously enough, the 1S series calculations seem to be somewhat better. This is probably partly due to the fact that the S series is a rather pure Rydberg series with very little cor-

relation and partly due to the mixing of the $2snp$ series with $2p3s$, which has not quite been fully accounted for. At any rate, both the 3P and 1P terms of $2p3p$ appear to be calculated quite well, within 60 and 70 cm^{-1} of experiment, respectively, providing the $3455\text{-}\text{\AA}$ line is interpreted as the $2s3p^1P - 2p3p^1P$ transition. The wavelength of this transition computed directly from the theoretical total energies is 3459 \AA . This assignment thus places the $2p3p^1P$ at $89\,121 \text{ cm}^{-1}$ above the ground state.

In order to get an estimate of the lifetimes of these states the important branchings had to be estimated, so an approximate HF function (by way of the natural orbital technique) was computed for $2p3s^3P$. Since both the 3P and 1P of $2p3s$ are autoionizing states, correlation effects could not be rigorously calculated within the scope of the procedures used here. The 1P was neglected, since it has been calculated by Altick¹⁵ to lie 0.16 eV above the triplet and its effect on the lifetime, due to the very long wavelength, was estimated to be negligible.

The results of the oscillator-strength calculations are given in Table V, which shows, not surprisingly, that the overwhelmingly predominant decay mode for both 3P and 1P is to $2s3p$. The predicted lifetimes are somewhat uncertain for two reasons, in addition to the residual correlation errors in the theoretical values. In the first place, the $2p3p$ states decay to the full $2snp$ discrete series as well as the lower $2skp$ continuum. These calculations stop at $2s4p$ and should thus give an upper limit to the lifetime, although most of the transition probability certainty seems to be due to just the one transition to $2s3p$. Secondly, the $2p3s$ levels interact with the continuum which shifts and broadens them in an unknown way. While

TABLE IV. Theoretical and experimental energies for the $1,^3P$ states of neutral beryllium. Theoretical term values are calculated relative to the appropriate Hartree-Fock (HF) limit.

		No. of configurations	Term Value				Expt. ^a (cm ⁻¹)
			E_{tot} (a. u.) HF	SOC	SOC (a. u.)	SOC (cm ⁻¹)	
Be I	$2s2p\ ^3P$	8	-14.51150	-14.51844	0.34104	52899	53212
	$\ ^1P$	27	-14.39473	-14.42355	0.14615	32074	32627
	$2s3p\ ^3P$	16	-14.34886	-14.35106	0.07366	16166	16284
	$\ ^1P$	21	-14.33139	-14.34456	0.06716	14740	15005
	$2s4p\ ^3P$	15	-14.31464	-14.31530	0.03790	8318	8380
	$\ ^1P$	13	-14.30894	-14.31413	0.03673	8061	8157
Be II	$2s\ ^2S$	1	-14.27740		0.0	0	0
Be I	$2p3p\ ^3P$	18	-14.16400	-14.19941	0.06856	15046	15108
	$\ ^1P$	6	-14.21181	-14.21257	0.08172	17934	(18004) ^b
	$2p3s\ ^3P$	1	-14.22592			20864	21567
Be II	$2p\ ^2P$	1	-14.13085		0.0	0	0

^aSee L. Johansson, Ref. 6.^bThis is based on classifying the 3455-Å line as $2s3p\ ^1P - 2p3p\ ^1P$.

the effect of the $2p3s$ autoionizing states on these lifetimes appear to be small, this must still be counted an open question here. At least the computed lifetimes, for both the 3P and 1P , are consistent with the values recently measured by the beam-foil technique.^{1-3,7}

The wavelengths listed in Table V, and used to calculate f and A , are the experimental values. For the singlets these wavelengths are computed on the assumption that the $2p3p$ level is located $89\ 121\ \text{cm}^{-1}$ above the ground state. This results in a prediction of two weak lines at 2148 and $4528\ \text{Å}$, which have previously not been noted in the beryllium spectrum. Recently, however, weak lines at approximately these wavelengths have been found in beam-foil spectra,⁷ which lends further support for the proposed classification.

IV. SUMMARY AND CONCLUSIONS

To summarize then, fairly-large-scale CI calculations have been done on the $2sns\ ^1S$ series of

beryllium through $7s$. These calculations also appear to have the potential to represent most of the correlation effects in states such as $2s^2$ and $2p^2$. The results indicate that, except for the ground state, the lowest six s states are overwhelmingly Rydberg in nature. The $2p^2\ ^1S$ is not found between $6s$ and $7s$, where it had previously been assigned, based on identifying the 3455-Å line as $2p^2\ ^1S - 2s2p\ ^1P$.

Further variational calculations on the $2snp$ and $2p3p$ levels indicate that this line should be reassigned as the $2s3p\ ^1P - 2p3p\ ^1P$ transition. Both the calculated lifetimes and the predicted spectral lines are consistent with all currently available data.

With this reassignment scheme the question of the location of the $2p^2\ ^1S$ level still remains. While this question has not been definitively answered by these calculations, there is the suggestion that the $2p^2$ is $\approx 0.23\ \text{eV}$ above the ionization limit. If so, it would be an autoionizing state and may be unob-

TABLE V. Oscillator strengths, transition probabilities, and lifetimes for Be I. Wavelengths are the experimental values, with the singlet wavelengths based on reassigning the 3455-Å line.

Transition	λ (Å)	Oscillator Strength				A ($10^8\ \text{sec}^{-1}$)		τ (nsec)		Expt. τ (nsec)
		HF		SOC		len.	vel.	len.	vel.	
$2s2p\ ^3P - 2p3p\ ^3P$	1428	0.007	0.002	0.0	0.0	0.001	0.001	7.10	6.47	6.9 ± 1.0^a
$2s3p - 2p3p\ ^3P$	3020	0.159	0.073	0.175	0.198	1.28	1.45			
$2s4p - 2p3p\ ^3P$	3968	0.002	0.002	0.001	0.002	0.002	0.008			
$2p3s - 2p3p\ ^3P$	15480	0.448	0.314			0.125	0.087			
$2s2p\ ^1P - 2p3p\ ^1P$	2148	0.070	0.017	0.0002	0.0001	0.002	0.001	6.69	6.11	$5.0 \pm 0.2,^b$ $5.35 \pm 0.14,^c$ 5.4 ± 0.2^d
$2s3p - 2p3p\ ^1P$	3455	0.140	0.183	0.247	0.278	1.38	1.55			
$2s4p - 2p3p\ ^1P$	4528	0.003	0.008	0.034	0.027	0.112	0.087			

^aBerry *et al.*, Ref. 7.^bAndersen *et al.*, Ref. 1.^cBergstrom *et al.*, Ref. 2.^dBromander, Ref. 3.

servable spectroscopically. Probably the best hope of settling the matter lies with calculations

which include directly the effects of coupling with the continuum, such as those of Altick.¹⁵

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Calculations of Effusive-Flow Patterns. I. Knudsen-Cell Results*

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A simple and direct procedure has been used to calculate the flux gradients inside Knudsen cells and the related effusive-flow patterns. Knudsen cells of simple geometries with knife-edge orifices and flat sources are considered. The calculated value of the Motzfeldt factor (1.020) is in very good agreement with the literature value (1.020) and the Monte Carlo calculations (1.020) for a cell of reduced height $H=4.0$ and the knife-edge orifice of reduced diameter=0.1064. It is suggested that an extension of these calculations has an importance in solving some of the problems encountered in determining the absolute total scattering cross section from scattering measurements.

INTRODUCTION

The statistics of molecular dynamics and spatial distribution for gases at equilibrium are well understood. Experiments with gases, however, often involve mass flows having non-Maxwellian distributions which, depending on the magnitudes and directions of the gradients, are more or less difficult to characterize. The internal geometry of the apparatus influences the details of mass-flow distributions. The effects of orifice shapes, in particular, on such distributions have been widely studied for all types of flows from free molecular effusions to supersonic jets. Generally, less attention has been given to the effects of over-all apparatus geometry including the location of tubulations, chamber walls, and internal structures on flow characteristics. At high pressures the conducting apertures and channels have the greatest influence on gas-flow patterns, but at low pressures the arrangement of other fixed surfaces becomes increasingly important, and when gas mole-

cules collide with apparatus surfaces more frequently than with other molecules in the vapor phase the flow pattern is very sensitive to the detailed arrangement of those surfaces.

The latter situation arises in effusive flows, and any adequate description of flow patterns and density gradients in these cases will depend on the over-all geometry of the flow system and not just that of the apertures. Obtaining such descriptions by straightforward solution of Boltzmann's integrodifferential equation or Maxwell's equation of change with explicit inclusion of gas-surface interactions would be very difficult, but indirect methods are more or less practical depending on the complexity of the system. These methods are substantially simplified if gas reflection by the fixed surfaces is assumed to be diffuse since such reflection momentarily restores certain equilibrium conditions to the molecular stream reflected from a surface element.

Most treatments of effusive flow have used this simplification since the classic work of Clausing¹