Brief Reports

Multiconfiguration Hartree-Fock calculations of the oscillator strength for the $2s2p$ $^1P° \rightarrow 2p^2, 2snd$ ^1D $(n=3-6)$ transitions in beryllium

H. P. Saha*

Supercomputer Computations Research Institute, Florida State University, Tallahassee, Florida 32306-4052

C. Froese Fischer

Department of Computer Science, Vanderbilt University, Nashville, Tennessee 37235

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The multiconfiguration Hartree-Fock method has been applied successfully to the calculation of oscillator strength for the transitions $2s2p$ $^1P° \rightarrow 2p^2, 2snd$ ^1D $(n=3-6)$ in beryllium. The effects of electron correlation, which are very important for these calculations, have been taken into account accurately through the configuration-interaction procedure. The length and velocity results of the oscillator strength as well as the calculated and experimental transition energies are in excellent agreement. The present results compare well with experiment and other available theoretical data.

I. INTRODUCTION

Oscillator strengths or transition probabilities of the Rydberg states of alkaline-earth elements have importance in astrophysics and present difficulties for both theoreticians and experimentalists. Over the past few years energy levels and oscillator strengths of the Rydberg states of alkaline-earth elements have been investigated by various methods. Perturbations of atomic Rydberg series by a single foreign term or perturber have been known for a long time[1−12] in atomic spectroscopy where they produce anomalous behavior in the quantum defects and term splitting along the series. Energy levels and oscillator strengths are very sensitive to the correlation part of the electronic wave function. In order to obtain accurate results within the experimental error of beam-foil lifetime measurements, the effect of electron correlation in the initial and the final states of the $2s2p$ $^1P° \rightarrow 2p^2, 2snd$ ^1D $(n=3-6)$ transitions must be considered very carefully and systematically. Many publications are found on the experimental[1,2] and theoretical results[3−8] of oscillator strengths for such transitions in beryllium. Both calculated and experimental values vary rather considerably. Experimental measurements are generally based on measuring the lifetime of an excited state using beam-foil techniques. The reliability of the experimental data depends on the importance of cascade effects. Many calculations[3−8] using different methods have been carried out to take into account electron correlation effects to study the systematic behavior of the oscillator strength for the $2s2p$ $1P° \rightarrow 2p^2, 2snd$ ^1D $(n=3-6)$ transitions in beryllium.

Nicolaides *et al.*[4] calculated the oscillator strength for the $2s2p$ $^1P° \rightarrow 2p^2$ ^1D line of beryllium using wave functions containing all of the specifically nonclosed-shell type of correlation effects given by Sinanoglu's[13] nonclosed-shell many-electron theory (NCMET). Hibbert[6] used a configuration-interaction (CI) wave function to obtain an absorption oscillator strength using both the length and the velocity forms for transition $2s2p$ $^1P° \rightarrow 2p^2$ ^1D. He included both L shell and K-L intershell correlations in the calculations. Moser *et al.*[7] computed the oscillator strength for the transition $2s2p$ $^1P° \rightarrow 2p^2, 2snd$ ^1D by applying variational Bethe-Goldstone equations.[14] Victor and Laughlin[5] applied the semiempirical model potential method to the calculation of wavelengths and oscillator strengths for the transitions $2s2p$ $^1P° \rightarrow 2p^2, 2snd$ ^1D $(n=3-6)$ in beryllium. Their model potential contains the effect of virtual polarization of the $1s^2$ core. Weiss[3] carried out large-scale configuration-interaction calculations on the transitions between states in beryllium. Nicolaides and Beck[8] applied the first-order theory of oscillator strengths (FOTOS) to the calculation of oscillator strengths for the transitions $2s2p$ $^1P° \rightarrow 2p^2, 2snd$ ^1D $(n=3-6)$. They placed much emphasis on the accurate prediction of the transition matrix element and not on the exact Schrödinger equation for the initial- and the final-state wave functions. They treated the Fermi sea (FS) of orbitals as the zeroth-order vectors for the initial and the final states. These FS vectors were used to evaluate the transition operator and then additional correlation effects in the initial and the final states were selected which contribute to the transition amplitude. These correlations

were expressed in terms of the Hartree-Fock and variational optimized virtual orbitals for each state. A comparison of these theoretical results[3-8] with experimental data[1,2] shows that there is still a certain discrepancy among various theoretical (experimental) results and also between theory and experiment. As a result, there is a need for a systematic and careful study of this problem with a very accurate method.

The multiconfiguration Hartree-Fock (MCHF) method which can efficiently take into account electron correlation effects in the ground and the excited states has been known for a long time to obtain accurate results for transition energies, allowed and forbidden transition probabilities of astrophysical importance in carbon and oxygen, and their isoelectronic sequences.[15-17] In the present paper we report results of a systematic study of oscillator strengths applying the MCHF method taking electron correlation effects into account very carefully, but omitting spin-orbit effects and other relativistic corrections.

Theoretical treatment of the transitions $2s2p\ ^1P^\circ \rightarrow 2p^2, 2snd\ ^1D$ $(n=3-6)$ is complicated by a strong interaction of the $2p^2\ ^1D$ configuration state with the $2snd\ ^1D$ Rydberg series. Since the wave-function composition is important for oscillator strength predictions, wave functions for the initial and the final states must be calculated accurately. Froese Fischer[11] made a very careful study for the $2p^2, 2snd$ $(n=3-6)$ low-lying ^1D states of beryllium. It was shown that if the electron correlation effects are treated accurately and carefully, energy levels are found to be in the designated order in contrast to Hartree-Fock (HF) results. The generally accepted labeling of the ^1D states in beryllium is appropriate in that the lowest ^1D, though mixed, is predominantly of $2p^2\ ^1D$ character, the second largely $2s3d$, and the third almost entirely $2s4d$.

Since the primary goal here is to obtain as accurate an approximation as possible for the wave function and energies, each state was treated independently by separate MCHF calculations.[18] All calculations were performed using an MCHF atomic structure software package[19] that allows for non-orthogonal orbitals both within an MCHF calculation and in the calculation of oscillator strengths.[20]

II. INITIAL-STATE WAVE FUNCTION

The MCHF wave function expansion for the $2p^2, 2snd\ ^1D$ $(n=3-6)$ series are the same as in the earlier paper.[11] In this approximation the wave function for the

first three states $2p^2$, $2s3d$, and $2s4d$ were expressed as a linear combination over the set of configuration states,

$$\{2p_1^2, 3p_1^2, 3d_2^2, 4d_2^2, 4f_2^2, 5f_2^2, 2p_2 4f_1, 3p_2 5f_1, 2s3d_1 ,$$

$$2s4d_1, 5d_2^2, 5g_2^2, 3d_4 5g_4, 3s3d_3, 4s4d_3, 2p_1 3p_3\}\ ^1D ,$$

where subscripts, when present, are used to designate different orbitals of the indicated type. Orbitals with the same subscript constitute an orthonormal set. For stability the $2s$ and $3d$ orbitals of the $2s3d$ configuration were fixed at their Hartree-Fock values and the $4d$ orbital was determined variationally to represent the rest of the Rydberg series. The $3d$ orbital of $3s3d$ was not constrained to be the same as the Hartree-Fock orbital of $2s3d$ and indeed was much more contracted. All the orbitals, with the exception of $1s$, $2s$, and the Hartree-Fock $3d$ orbitals, were varied individually for these three states. For the $2s5d\ ^1D$ state we add this configuration to the above set and for the $2s6d\ ^1D$ state we add $2s6d$ and $2s5d$ to the above set of configurations and all the orbitals except $1s$, $2s$, $3d$, $4d$, and, in the latter case, also $5d$ were varied individually for these two states.

To improve the energy-level prediction further it was necessary to include both correlation between the outer two electrons and the core and correlation with the core. In the two separate calculations, orbitals

$$2s_j, 4p_j, 2p_i, 3d_i, 3s, 2p_0, 3p_0$$

were determined representing the interaction of $1s2s_j 2p_1 4p_j$ and $1s2p_i 3d_i 2p_1$ with the perturber $2p^2$ and the interaction of $1s2s3s3d_1$, $1s3s^2 3d_1$, $1s2p_0 3p_0 3d_1$, and $1s3p_0^2 3d_1$ with $2s3d$. The following configurations

$$\{1s2s_j 2p_1 4p_j, 1s2p_i 3d_i 2p_1, 1s2s3s3d_1 ,$$

$$1s3s^2 3d_1, 1s2p_0 3p_0 3d_1, 1s3p_0^2 3d_1, 1s2s3s4d_1 ,$$

$$1s3s^2 4d_1, 1s2p_0 3p_0 4d_1, 1s3p_0^2 4d_1\}\ ^1D ,$$

were added to the expansion list for the perturber $2p^2$ and $2snd$ Rydberg series given earlier but in the interaction matrix, the interactions between $1s2p_i 3d_i 2p_1$ and $1s2p_0 3p_0 3d_1$, $1s3p_0^2 3d_1$, $1s2p_0 3p_0 4d_1$, $1s3p_0^2 4d_1$ were omitted. This approximates a first-order calculation.

III. FINAL-STATE CONFIGURATION

The MCHF expansion for the final state $2s2p\ ^1P^\circ$ was over the following set of configurations:

$$\{2s_1 2p_1, 3s_1 3p_1, 2p_2 3d_2, 3p_2 4d_2, 3d_3 4f_1, 4s_1 4p_1, 4d_3 5f_1, 4f_2 5g_1, 5f_2 6g_1, 4p_2 5d_2 ,$$

$$5s_1 5p_1, 1s2s_1^2 2p_1, 1s2s_1 2p_1 3s_1, 1s2s_1 2p_1 3d_1, 1s2p_2^2 3p_2, 1s2s_1^2 3p_1, 1s2p_1 3s_1^2, 1s2p_2 3p_2^2\}\ ^1P^\circ ,$$

where $1s^2$ has been omitted in the two-electron configuration. This configuration set also includes correlations with the core. All the orbitals except $1s$ were varied simultaneously to obtain an accurate energy. The $1s$ orbital was obtained from a Hartree-Fock calculation of the $2s2p\ ^1P^\circ$ state.

IV. RESULTS AND DISCUSSIONS

In Table I we have presented the total energy relative to the $2s\ ^2S$ ionization limit for two different approximations. In the first column of energies, are the Hartree-Fock energies. In the Hartree-Fock approximation, the

TABLE I. Total energies (in atomic units), relative to the 2s ^2S ionization limit, for two different approximations.

State	HF	Correlated	Observed[a]
$2p^2\,^1D$	−0.025 41	−0.083 19	−0.085 48
$2s3d\,^1D$	−0.055 17	−0.048 79	−0.049 05
$2s4d\,^1D$	−0.031 06	−0.029 08	−0.029 21
$2s5d\,^1D$	−0.019 90	−0.019 07	−0.019 09
$2s6d\,^1D$	−0.013 83	−0.013 40	−0.013 40
$2s2p\,^1P°$	−0.117 33	−0.147 39	−0.148 68

[a]Reference 19.

$2p^2$ energy level is higher even than that of $2s4d$. The $2p^2$ electron distribution describes a compact, localized distribution of charge density, whereas the Rydberg series consists primarily of a contracted $2s$ electron and diffuse d electrons, whose mean radii increase rapidly with the principal quantum number n. In the second column of energies, we report the energy of the localized perturber $2p^2\,^1D$ and the members of the $2snd\,^1D$ Rydberg series and $2s2p\,^1P°$ state, when correlation was included. Correlated energies are in excellent agreement with observation.[21]

In Table II, we have tabulated oscillator strengths for beryllium $2s2p\,^1P°{\rightarrow}2p^2,2snd\,^1D$ $(n=3-6)$ transitions. In this table we also presented results obtained by other methods[3−8] and by experiments.[1,2] The wave functions for the initial and the final states described earlier are used to calculate length and velocity oscillator strength values for the corresponding $^1P°{\rightarrow}\,^1D$ transitions. The oscillator strength for the $2s2p\,^1P°{\rightarrow}2p^2\,^1D$ transition is very small. The agreement between the dipole length and velocity oscillator strength for this transition is excellent considering the extensive cancellation that is present. Comparison with experimental results shows good agreement, though the experimental value is higher. The results obtained by Hibbert[6] for this transition with configuration-interaction calculations are a factor of 2 smaller than the present results, and the length and velocity results also show good agreement. Nicolaides et al.[4] calculated the oscillator strength for this transition using nonclosed-shell many-electron theory. Moser et al.[7] calculated the oscillator strength for this transition by applying variational Bethe-Goldstone equations.[14] Their oscillator

strength is nearly zero for this transition. Weiss[3] carried out large-scale configuration-interaction calculations for the transitions $2s2p\,^1P°{\rightarrow}2p^2,2snd\,^1D$ $(n=3-6)$. His result for the transition $2s2p\,^1P°{\rightarrow}2p^2,2snd\,^1D$ compares well with our present results. Nicolaides and Beck[8] also calculated the oscillator strength for the transitions $2s2p\,^1P°{\rightarrow}2p^2,2snd\,^1D$ $(n=3-6)$ with the use of the first-order theory of oscillator strengths. Their velocity result for the $2s2p\,^1P°{\rightarrow}2p^2\,^1D$ is in excellent agreement with our length result. Their length result for this transition is five times larger than their velocity result. Experiment has provided only an upper bound for this oscillator strength. All of these theoretical results, though differing by orders of magnitude, are below the upper bound.

Victor and Laughlin[5] used the semiempirical model potential method to calculate oscillator strengths for the series of transitions $2s2p\,^1P°{\rightarrow}2p^2,2snd\,^1D$ $(n=3-6)$ in beryllium. Their result for the transition $2s2p\,^1P°{\rightarrow}2p^2\,^1D$ agrees well with the FOTOS length result of Nicolaides and Beck,[8] but is much higher than our present results. The present length and velocity results for the series of transitions $2s2p\,^1P°{\rightarrow}2snd\,^1D$ $(n=3-6)$ are in excellent agreement. They compare very well with the configuration-interaction results of Weiss.[3] The results obtained by Victor and Laughlin[5] using the model potential method agree well for $n=3$ but become larger than the present (and Weiss) as n increases. The length and velocity results for these transitions obtained by Nicolaides and Beck[8] do not agree as well as those for the present results. Particularly for $2s2p\,^1P°{\rightarrow}2s3d\,^1D$, the discrepancy is large (for $2s6d$ there are not enough significant digits to comment). The FOTOS calculations in beryllium performed by Nicolaides and Beck[8] are not complete and the results are given only to present a global description of the ^1D series. Only two experimental studies have been reported. Anderson et al.[2] determined the oscillator strength for these transitions from the lifetime measurements using the beam-foil technique. Bergstrom et al.[1] obtained the oscillator strength for the transitions $2s2p\,^1P°{\rightarrow}2snd\,^1D$ $(n=3,4)$ from their beam-foil lifetime measurements. The two common results differ appreciably. The results obtained by Bergstrom et al.[1] are smaller than those obtained by Anderson et al.[2] The results of the present calculation are in excellent agreement with the experimental measurements of Bergstrom et al.[1] but slightly smaller than the larger experimental values of An-

TABLE II. Oscillator strengths for the Be $2s2p\,^1P°{\rightarrow}2p^2,2snd\,^1D$ transitions.

State	Present work f_L	f_V	FOTOS[a] f_L	f_V	CI[b] f_L	f_V	NCMET[c] f_L	f_V	Bethe-Goldstein[d] f_L	f_V	CI[e]	Model Pot.[f]	Expt. Ref. 2	Ref. 1
$2p^2\,^1D$	0.0016	0.0010	0.0086	0.0016	0.000 65	0.000 47	0.020	0.016	0.0003	0.0000	0.001	0.0084	<0.048[g]	
$2s3d$	0.404	0.425	0.64	0.41							0.41	0.418	0.50	0.43
$2s4d$	0.1808	0.1898	0.19	0.16							0.173	0.191	0.25	0.19
$2s5d$	0.0793	0.0819	0.08	0.07							0.081	0.090	0.16	
$2s6d$	0.0445	0.0454	0.05	0.05							0.043	0.050	0.07	

[a]Reference 8.
[b]Reference 6.
[c]Reference 4.
[d]Reference 7.
[e]Reference 3.
[f]Reference 5.
[g]There is a misprint of this result in Refs. 5 and 8.

derson *et al.*[2] It should be mentioned that Anderson *et al.*[2] did not consider the other decay channels except the strongest one $2s2p$ $^1P°{\rightarrow}2snd$ ^1D in converting their measured lifetimes to oscillator strengths. Other decay channels, e.g., $2s3p$ $^1P°{\rightarrow}2snd$ ^1D and $2s4f$ $^1F^0{\rightarrow}2snd$ ^1D, have been ignored in obtaining oscillator strengths, which might explain the significantly larger experimental f values and hence the difference between the theory and the experiment for the higher n values.

V. CONCLUSION

Careful and extensive calculations of oscillator strength for several transitions in beryllium have been presented. The multiconfiguration Hartree-Fock method, which takes into account electron correlation effects, has been applied in these calculations. The main emphasis is on obtaining accurate wave functions for both the initial and the final states resulting in the excellent agreement not only between the calculated and the experimental transition energies, but also in agreement between the length and velocity values for the oscillator strengths. Generally the present results agree with other theoretical data. There is good agreement with the experimental results reported by Bergstrom *et al.*[1] but quantitative agreement with the more extensive data presented by Anderson *et al.*[2] is lacking.

*To whom correspondence should be made.

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