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Energy levels and lifetimes for some quartet states of Be II

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Multiconfiguration Hartree-Fock calculations have been performed for many doubly excited quartet states of Be II. Total energies and lifetimes are reported as well as wavelengths and f values for transitions between states. The calculations support many, though not all, recent assignments.

I. INTRODUCTION

The doubly excited $1s2snl$ and $1s2pnl$ quartet states of Be II have been the subject of several recent publications.[1-5] These states are readily populated in beam-foil experiments but the analysis, particularly of the earlier experiments, was hampered by limited resolution (see, e.g., the reviews of Berry[6] and To *et al.*[7]). The more recent experiments[2,3] have improved the accuracy of previously available data and also have provided additional data. Theoretical calculations of energies and transition probabilities have played a vital role in the classification of this data. Indeed, in their recent paper, Bentzen *et al.*[4] emphasize the importance of the interplay between precise theoretical calculations and experimental data in the analysis of the Be II spectrum. Both wavelengths and lifetimes were factors in the classification of the lines.

Precise energy level calculations have been performed by Larsson *et al.*[8] for some $2sns\,^4S$ and $2snp\,^4P^o$ states and by Lunell and Beebe[9] for $2s2p\,^4P^o$ and also $2p^2$, $2p3p\,^4P$, though transition probabilities were not reported. Calculations to spectroscopic accuracy have been reported by Galán and Bunge[1] for certain key states—$2s3d\,^4D$, $2p3d\,^4D^o$, $\{2s4f,2p3d\}^4F^o$, and $2p4f\,^4F$—and these have contributed substantially to the understanding of the quartet system. Both wavelengths and f values were reported. The most recent calculations are Laughlin's[5] model potential calculations. Although not as accurate as the calculations mentioned earlier, they have led to the reassignment of some lines as well as some new assignments by Bentzen *et al.*[4]

The quartet system in Be II is an interesting one from a theoretical point of view. Three-electron systems are simple enough that a fairly high level of accuracy is attainable without the problem becoming overwhelming. The important correlation effects are between the outer two electrons and, to a good approximation, the three-electron system may be treated as a two-electron system outside a $1s$ core.

The multiconfiguration Hartree-Fock (MCHF) method is particularly effective for two-electron systems[10] and special procedures have been studied to deal with a perturber embedded in a Rydberg series.[11] Programs are under development that, in the present case, will simplify the inclusion of not only outer correlation, but also correlation of an outer electron with the $1s$ electron. In their calculations Galán and Bunge include radiative and mass polarization corrections and estimate relativistic effects in a semiempirical manner. Although spin-orbit interaction is not expected to be large there is a larger relativistic shift correction (LS dependent only) for $1s2snl$ configurations than for $1s2pnl$ configurations and this may affect the energy difference between two configurations. A modified version of the MCHF77 program includes these effects in the diagonalization process.

The present study was undertaken to evaluate the MCHF techniques being developed for atomic structure calculations, to assess the level of accuracy that can be achieved, and to assist the identification of observed lines. Particular attention has been given to more highly excited states where fewer theoretical studies have been performed.

II. The MCHF Calculations

As in a configuration interaction (CI) calculation an MCHF wave function Ψ for a state, γLS, is expressed as a linear combination of configuration state functions $\Phi(\alpha LS)$, i.e.,

$$\Psi(\gamma LS)=\sum_i c_i\Phi(\alpha_i LS)\ ,$$

where γ is a label for the state (usually the dominant component) and α a label for the configura-

TABLE I. Wave-function expansions used in MCHF calculations for states in Be II.

State	Configuration expansion
$2s2p\ ^4P^o$	$1s2s_12p_2, 1s3s_13p_2, 1s2p_13d_1, 1s3d_24f_2, 1s4f_15g_1, 2s_33s_32p_2, 3p_34p_32p_2, 3d_34d_32p_2, 2s_i2p_i2s_1, 2p_j3d_j2s_1, 3d_k4f_k2s; 2p_i$ and $2p_j \perp 2p_2$
$2p^2\ ^4P$	$1s2p_1^2, 1s3p_1^2, 1s3d_1^2, 1s4f_1^2, 2s3p_22p_2, 3p_33d_32p_3, 1s4p_1^2, 1s4d_1^2, 2s2p_2^2, 3d_44f_42p_1$
$2s3s\ ^4S$	$1s2s_13s_1, 1s2p_13p_1, 1s3d_14d_1, 2s_i2p_i3p_1, 2p_j3d_j3p_1, 2s_k3s_k3s_1, 2p_k3p_k3s_1$
$2s3p\ ^4P^o$	(same as $2s2p\ ^4P^o$ but with $2p_2$ and $3p_2$ interchanged)
$2s3d\ ^4D$	$1s2s_13d_1, 1s2p_13p_1, 1s3s_14d_1, 1s3d_25g_2, 1s2p_24f_2, 2p_i3p_i3d_1, 4d_j5d_j3d_1, 1s4p_15p_1, 1s4d_33d_3, 4s_i3s_i3d_1; 4s_i$ and $3s_i \perp 2s_1$
$2p3s\ ^4P^o$	$1s2p_23s_1, 1s3p_22s_1, 1s2p_13d_1, 1s3p_14d_1, 1s3d_24f_2, 2s_i2p_i3s_1, 2p_j3d_j3s_1, 3s_i3p_i3d_1, 3p_j4d_j3d_1; 3s_i \perp 3s_1$
$2s4s\ ^4S$	(same as $2s3s\ ^4S$ but with $3s_1$ replaced by $4s_1$)
$2p3p\ ^4D$	(same as $2s3d\ ^4D$, adding $1s2s_14d_1, 1s3s_13d_1, 1s2p_14p_1, 1s3p_14p_1, 2s_k2p_k3p_1, 2p_m3d_m3p_1$ and omitting $1s4p_15p_1$)
$2s4p\ ^4P^o$	(same as $2s3p\ ^4P^o$ but with $3p_2$ replaced by $4p_2$)
$2s4f\ ^4F^o(1)$ and $2p3d\ ^4F^o(2)$	$1s2p_13d_1, 1s3p_14d_1, 1s3d_24f_2, 1s4f_15g_1, 1s2s_34f_3, 1s3s_35f_3, 2s_i2p_i3d_1, 2p_j4d_j3d_1, 4d_k4f_k3d_1, 2s_43s_44f_3, 2p_43p_44f_3, 3d_44d_44f_3; 2s_4$ and $3s_4 \perp 2s_3, 3d_4 \perp 3d_1$
$2p3p\ ^4S$	$1s2p_13p_1, 1s2s_13s_1, 1s3d_14d_1, 2s_i2p_i3p_1, 2p_j3d_j3p_1, 2s_k3s_k3s_1, 2p_k3p_k3s_1$
$2s4d\ ^4D$	(same as $2s3d\ ^4D$ with $3d_1$ replaced by $4d_1$ and $1s2s_13d_1, 1s3s_13d_1$ added)
$2p3p\ ^4P$	$1s2p_13p_1, 1s2p_1^2, 1s3p_14p_1, 1s3p_1^2, 1s3d_14d_1, 1s3d_1^2, 1s4p_1^2, 2s2p_2^2, 2s2p_23p_1, 2p_33d_33p_1$
$2p3d\ ^4D^o$	$1s2p_13d_1, 1s3p_14d_1, 1s3d_24f_2, 1s4f_15g_1, 2s_i3p_i3d_i, 2p_j4d_j3d_j, 4d_k4f_k3d_1$
$2p3d\ ^4P^o$	$1s2p_13d_1, 1s3p_14d_1, 1s2s_12p_2, 1s2s_13p_2, 1s3s_12p_2, 1s2s_14p_2, 1s3s_13p_2, 1s3d_24f_2, 1s4f_15g_1, 2s_i3p_i3d_1, 2p_j4d_j3d_1, 4d_k4f_k3d_1, 2s_33s_34p_2, 2p_33p_34p_2, 3d_34d_34p_2; 2p_j \perp 4p_2$
$2s5g\ ^4G$	$1s2s_15g_1, 1s3s_16g_1, 1s3d_14d_1, 1s4f_25f_2, 1s3d_25g_2, 1s2p_14f_1, 2s_43s_45g_1, 2p_43p_45g_1, 3d_44d_45g_1; 2s_4$ and $3s_4 \perp 2s_1$
$2s5f\ ^4F^o$	[same as $^4F^o(1)$ and $^4F^o(2)$ but with $4f_3$ and $5f_3$ interchanged and $1s2s_34f_3$ added]
$2s6f\ ^4F^o$	(same as $2s5f\ ^4F^o$ but with $5f_3$ replaced by $6f_3$)
$2p4s\ ^4P^o$	$1s2p_24s_1, 1s2p_13d_1, 1s2p_14d_1, 1s3d_24f_2, 2s_i2p_i4s_1, 2p_j3d_j4s_1, 1s2p_23s_1, 1s3p_33s_1, 1s2s_1np_2$, $n=2$ to 9
$2p4p\ ^4D$	$1s2p4p, 1s2s_14d_1, 1s3d_24d_2, 2s_i3p_14p_1, 2p_j3d_j4p_1, 3s_14s_14d_1, 2p_33p_34d_1; 3d_j \perp 4d_1$
$2p4p\ ^4P$	$1s2p_14p_1, 1s2p_1^2, 1s3p_15p_1, 1s3p_1^2, 1s3d_14d_1, 1s3d_1^2, 2s2p_2^2, 2s2p_24p_1, 2p_33d_34p_1$
$2p4d\ ^4F^o$	$1s2p_14d_1, 1s2p_13d_1, 1s3p_1, 3d_1, 1s3d_24f_2, 1s4f_15g_1, 2s_i3p_i4d_1, 2p_j3d_j4d_1, 4d_k4f_k4d_1, 1s2snf$, $n=4$ to 13
$2p4d\ ^4D^o$	(same as $2p3d\ ^4D^o$ but with $3d_1$ and $4d_1$ interchanged)
$2p4f\ ^4F$	$1s2p_14f_1, 1s3p_15f_1, 1s3d_1^2, 1s3d_14d_1, 1s4f_2^2, 1s4f_25f_2, 1s3d_25g_2, 2s_i3p_i4f_1, 2p_j4d_j4f_1, 4d_k5f_k4f_1$
$2p4d\ ^4P^o$	$1s2p_14d_1, 1s3p_13d_1, 1s3d_24f_2, 1s4f_15g_1, 2s_i3p_i4d_1, 2p_j4p_j4d_1, 4d_k4f_k4d_1, 1s2s_1np_3$, $n=2$ to 9 and $1s2p_3ns_1$, $n=3$ to 5
$2p4f\ ^4G$	(same as $2p4f\ ^4F$ omitting $1s3d_1^2, 1s4f_2^2$ and adding $1s2sng$, $n=5$ to 14)
$2p4f\ ^4D$	$1s2p_14f_1, 1s3p_15f_1, 1s3d_14d_1, 1s4f_25f_2, 1s3d_25g_2, 2s_i3p_i4f_1, 2p_j4d_j4f_1, 4d_k4f_k4f_1, 1s2s_1nd$, $n=3$ to 9
$2p5f\ ^4F$	(same as $2p4f\ ^4F$ but with $4f_1$ and $5f_1$ interchanged)
$2p5g\ ^4G^o$	$1s2p_15g_1, 1s3p_16g_1, 1s3d_14f_1, 1s4f_25g_2, 2s_i3p_i5g_1, 2p_j3d_j5g_1, 4d_k4f_k5g_1$
$2p6f\ ^4F$	(same as $2p5f\ ^4F$ but with $5f_1$ replaced by $6f_1$)

tion. Configurations in the expansion are selected to represent various correlation effects. For outer correlation, a reference configuration is selected, namely, the configuration with the expected dominant component, and all single and double replacements of the outer electrons are considered. For example, allowed replacements from $2s3d\ {}^3D$ lead to the set of configurations

$$\{2s3d,ns3d,2snd,nsnd,mpm'p,ndn'd;n\geq 3,\ m\geq 2\}^3D\ .$$

Sums over these configurations may be reduced[10] through transformations of the orbital basis to the smaller set

$$\{2s_1 3d_1,3s_1 4d_1,\ldots,2p_1 3p_1,4p_1 5p_1,\ldots,3d_2 4d_2,5d_2 6d_2,\ldots;\ldots\}^3D\ ,$$

where orbitals for electrons with the same subscript (or set indicator) form an orthonormal set. Generally, each series with the same two-electron angular coupling converges fairly rapidly and only a few configurations need be considered. Extensive mixing of configurations becomes apparent at this stage of the calculation. For excited states higher than the lowest of their symmetry, the reduced form may be variationally unstable in which case other forms or special procedures must be used.[11]

To some extent, the motion of the outer electrons is also correlated with that of the $1s$ electron. In the calculations reported here we have assumed that the only important correlation is between the $1s2s\ {}^3S$ and $1s2p\ {}^3P$ pairs. A study of correlation in helium[10] leads to several conclusions.

(i) Correlation is smaller in the $1s2s\ {}^3S$ pair than the $1s2p\ {}^3P$ pair and therefore may affect a transition energy.

(ii) Most of the correlation effect is captured by the configuration $2p3p\ {}^3S$ for $1s2s\ {}^3S$ correlation and by $\{2s3p,2p'3d\}^3P$ for $1s2p\ {}^3P$ correlation.

(iii) The radial functions for the virtual, correlation orbitals are much more contracted than those for outer orbitals. Thus a different orbital basis is needed to capture the two types of correlation with a minimum set of configurations.

The present version of the MCHF program allows for such a nonorthogonal orbital basis. It only assumes that all orbitals *within* a configuration are orthonormal, and that all configuration states are orthonormal. The latter orthogonality condition is often satisfied by the angular coupling and so an appreciable degree of nonorthogonality of the radial orbitals is permitted. Such nonorthogonality introduces overlap integrals into the expression for the interactions. At present, angular programs are being developed to deal with limited nonorthogonality both for the determination of the interaction matrix, and the transition probability.[12] The MCHF program itself assumes the Slater integrals have at most one overlap integral raised to a power, and the one-electron integral

$$L_{nl,n'l}=\left\langle nl\left|\frac{d^2}{dr^2}+\frac{2Z}{r}-\frac{l(l+1)}{r^2}\right|n'l\right\rangle$$

at most two overlap integrals, each raised to a power. The present Be II calculations satisfy all these overlap constraints.

The wave-function expansions are presented in Table I. In these expansions the principal quantum number n does not play an important role except to denote that an orbital is different from other orbitals. The only exceptions are orbitals for dominant components (usually the first configuration) which are spectroscopic orbitals with the implied number of nodes. The subscript is the set indicator referred to earlier. In summary, the following orthogonality conditions apply: (i) All orbitals within a configuration are orthogonal, (ii) all orbitals within a specified set are orthogonal, (iii) all s orbitals are orthogonal to $1s$, and (iv) additional orthogonality as specified in Table I, the symbol $\perp$ denoting orthogonality.

III. WAVE FUNCTIONS AND TOTAL ENERGIES

The total energies, nonrelativistic (NR) and those with LS dependent relativistic shift corrections (R), including the mass-correction, Darwin term, and spin-spin contact term, are presented in Table II and compared with the most accurate values from other theories. Dominant wave-function expansion coefficients for states where strong mixing of configurations occurred are listed in Table III.

As Larsson *et al.*[8] reported earlier, $2p3s\ {}^4P^o$ and $2p3d\ {}^4P^o$ are both perturbers in the $2snp\ {}^4P^o$ Rydberg series. Our primary intent in repeating these calculations was to determine the energy of $2p3d{}^4P^o$ and obtain wave functions for some of these states so that transition probabilities and lifetimes could be computed. The present calculations for $2s3p\ {}^4P^o$ and $2s4p{}^4P^o$ represent stationary solutions with no explicit term in the expansion ensuring that the computed energy is an upper bound.

TABLE II. Total energies with (R) and without (NR) relativistic shift corrections for some states in Be II.

State	R	NR	Other theory (NR)
$2s2p\,{}^4P^o$	−10.067 57	−10.065 57	−10.066 41[f]
$2p^2\,{}^4P$	−9.872 07	−9.870 27	−9.868 36[g]
$2s3s\,{}^4S$	−9.621 51	−9.619 46	−9.619 49[f]
$2s3p\,{}^4P^o$	−9.570 72	−9.568 70	−9.568 93[f]
$2s3d\,{}^4D$	−9.542 55	−9.540 56	−9.540 92[h]
$2p3s\,{}^4P^o$	−9.477 52	−9.475 69	−9.475 74[f]
$2s4s\,{}^4S$	−9.464 23	−9.462 23	−9.461 69[f]
$2p3p\,{}^4D$	−9.448 62	−9.446 81	
$2s4p\,{}^4P^o$	−9.443 65	−9.441 65	−9.440 18[f]
$2s4f\,{}^4F^o(1)$	−9.437 11	−9.435 21	−9.435 79[h]
$2p3p\,{}^4S$	−9.431 86	−9.430 02	−9.428 11[f]
$2s4d\,{}^4D$	−9.430 74	−9.428 74[a]	
$2p3p\,{}^4P$	−9.429 18	−9.427 39	−9.423 97[g]
$2p3d\,{}^4F^o(2)$	−9.412 33	−9.410 42	−9.411 24[h]
$2p3d\,{}^4D^o$	−9.407 72	−9.405 93	−9.406 34[h]
$2p3d\,{}^4P^o$	−9.397 16	−9.395 32	
$2s5g\,{}^4G$	−9.379 54	−9.377 53	
$2s5f\,{}^4F^o$	−9.377 59	−9.375 59[b]	
$2s6f\,{}^4F^o$	−9.354 24	−9.352 24[b]	
$2p4s\,{}^4P^o$	−9.330 35	−9.328 54[c]	
$2p4p\,{}^4D$	−9.320 12	−9.318 25	
$2p4p\,{}^4P$	−9.313 72	−9.311 93	
$2p4d\,{}^4F^o$	−9.309 49	−9.307 71[d]	
	−9.308 80	−9.307 02[e]	
	−9.309 85	−9.307 93[c]	
$2p4d\,{}^4D^o$	−9.305 02	−9.303 24	
$2p4f\,{}^4F$	−9.303 63	−9.301 85	−9.302 14[h]
$2p4d\,{}^4P^o$	−9.303 57	−9.301 79[d]	
	−9.300 30	−9.298 51[e]	
$2p4f\,{}^4G$	−9.301 58	−9.299 80[d]	
	−9.299 69	−9.297 89[e]	
$2p4f\,{}^4D$	−9.300 68	−9.298 91[d]	
	−9.299 56	−9.297 78[e]	
$2s\,{}^3S$ limit	−9.299 05	−9.297 04	
$2p5f\,{}^4F$	−9.257 58	−9.255 80	
$2p5g\,{}^4G^o$	−9.256 92	−9.255 14	
$2p6f\,{}^4F$	−9.232 67	−9.230 89	

[a] Fixed $3d_1$.

[b] $3s_3, 4f_3$ fixed to their outer correlation value.

[c] Including all interactions with fixed, lower-lying members of the $2snp$ and $2pns$ Rydberg series.

[d] Omitting interactions with a $2snl$ Rydberg series.

[e] Including some interactions with a fixed $2snl$ Rydberg series.

[f] Reference 8.

[g] Reference 9.

[h] Reference 1.

Comparison with the Larsson *et al.* values shows that there is a slight downward drift and that our energy (NR) for $2s4p\,{}^4P^o$ is slightly lower than theirs. This may be attributed either to the stationary nature of our solution or to the decrease in accuracy of their method for the more diffuse states. The expansion for $2p3d\,{}^4P^o$ was considerably more elaborate than the one for $2snp\,{}^4P^o$, $n=2$ and 3. Here the $4p_2$ orbital was allowed to represent the interaction of $2p3d\,{}^4P^o$ with the whole $2snp_2$ Rydberg series, $n \geq 4$. Inspection of the interaction matrix showed that the diagonal energy of the $2s4p_2\,{}^4P^o$ configuration state was *above* that of the $2p3d\,{}^4P^o$ configuration state so, again, the solution is a stationary one rather than a strict upper bound. The $2p3d$ configuration is a fairly compact one and the larger interaction matrix elements (as distinct from effects on the wave function) are those associated with the $2s2p_2$ and $3s2p_2$ configurations. The interaction with $2s3p_2$ was already much smaller. Since these have been included explicitly in the wave-function expansion and since each contributes to the energy so as to raise the energy of the state, the $2p3d\,{}^4P^o$ is expected to be more accurate than the $2s4p\,{}^4P^o$ state. This is substantiated by a comparison of length and velocity forms of f values presented in Sec. IV.

TABLE III. Expansion coefficients for states with strong mixing of configurations. $\Psi(\alpha LS) = c_1\Phi(\alpha LS) + c_2\Phi(\alpha_2) + c_3\Phi(\alpha_3) + \cdots$, where $|c_2| > |c_3| > \cdots$.

γLS	α_2	α_3	c_1	c_2	c_3
$2s3p\,{}^4P^o$	$2p3d$	$2p3s$	0.983	0.148	0.109
$2p3s\,{}^4P^o$	$2p3d$		0.987	−0.150	
$2s4p\,{}^4P^o$	$2p3d$		0.984	0.179	
$2p3d\,{}^4P^o$	$2s4p$	$2s3p$	0.860	0.446	−0.182
$2p4s\,{}^4P^o$	$2s7p$	$2p4d$	0.923	−0.322	0.166
$2p4d\,{}^4P^o$	$2p4s$		0.948	0.262	
$2p3p\,{}^4S$	$2s3s$		0.909	0.415	
$2p3p\,{}^4P$	$2p^2$	$3p^2$	0.864	0.412	−0.278
$2p3p\,{}^4D$	$2s3d$	$2s4d$	0.945	0.306	−0.086
$2s3d\,{}^4D$	$2p3p$	$2p4f$	0.968	−0.226	−0.102
$2p4p\,{}^4D$	$2snd$		0.789	0.614	
$2s4f\,{}^4F^o(1)$	$2p3d$		0.720	0.693	
$2p3d\,{}^4F^o(2)$	$2s4f$		0.666	−0.745	
$2s5f\,{}^4F^o$	$2p3d$		0.979	−0.198	
$2s6f\,{}^4F^o$	$2p3d$		0.994	−0.111	
$2p4d\,{}^4F$	$2s12f$	$2s13f$	0.738	−0.440	0.440

The present nonrelativistic energy for $2p3p\,{}^4S$ is also seen to be lower than that of Larsson *et al.* The latter authors used the Hylleraas method which automatically gives upper bounds to every energy level, but the accuracy of the bound is expected to degrade for more loosely bound states. In our expansion of the wave function, the single $1s2s3s\,{}^4S$ configuration represents the interaction of $2p3p$ with the $2sns$ Rydberg series. In this case, the energy of the configuration state is lower than that of $2p3p$ and the interaction is such as to raise the energy of the state. A comparison of theoretical and experimental transition wavelengths for $2s2p\,{}^4P^o$-$2p3p\,{}^4S$ presented in Sec. IV suggests that, in this case, our total energy is the more accurate. MCHF calculations were also performed for $2s3s\,{}^4S$ and $2s4s\,{}^4S$. For the former, the MCHF energy is essentially the same as the value of Larsson *et al.* but for $2s4s\,{}^4S$ the MCHF energy is again lower. The present energies for $2p^2\,{}^4P$ and $2p3p\,{}^4P$ are both strict upper bounds, lower by 0.0019 and 0.0034 a.u., respectively, than the values obtained by Lunell and Beebe.[9]

Table III shows that there is considerable mixing of the configurations $\{2s3d,2p3p,2s4d\}^4D$ and, as already reported by Galán and Bunge, of $\{2s4f,2p3d\}^4F^o$. In fact, the $2s4f$ configuration state is dominant in both the lowest ${}^4F^o$ state and the second lowest. The states here are labeled $2s4f\,{}^4F^o(1)$ and $2p3d\,{}^4F^o(2)$, which, according to Table III, is clearly somewhat arbitrary. Galán and Bunge refer to them simply as ${}^4F^o(1)$ and ${}^4F^o(2)$. The present total energies are not as accurate as those of Galán and Bunge, being higher by 0.0003 to 0.0008 a.u. On the other hand, no extrapolation techniques have been used and relativistic effects have been computed in an *ab initio* manner.

Some comments are appropriate concerning the calculations for $2p4p\,{}^4S$, ${}^4D$, $2p4d\,{}^4P^o$, ${}^4F^o$, and $2p4f\,{}^4D$, ${}^4G$ states. All of these configuration states lie between high-lying members of a $2snl\,{}^4L$ Rydberg series. The Hartree-Fock energy for $2p4d\,{}^4F^o$, for example, is very close to that of $2s16f\,{}^4F^o$. Except for $2p4p\,{}^4D$, stationary wave functions could not be obtained when these interactions were included. On the other hand, it was noticed that during the course of the MCHF iterations, the *energy* did not vary appreciably and so a set of calculations was performed omitting these interactions. In order to evaluate the effect of interactions with the Rydberg series, a set of Hartree-Fock like orbitals were obtained from a calculation in which the $1s$ orbital was fixed to that of the first calculation and the $2snl$ orbitals determined so as to minimize $\sum E(1s2snl\,{}^4L)$, $n \leq 9$, except for $2p4f\,{}^5G$, where $n \leq 14$. A subsequent calculation, including interactions with these configuration states, was then performed. Only the orbital for the outer $4p$, $4d$, or $4f$ electron was varied. These energies (denoted by footnote e) also are included in Table II. As expected, the interaction with lower members of the Rydberg series, raised the energy of the perturber states. The remaining Rydberg series could raise the energy further but the neglected interactions with the continuum would lower the energy. Thus there is a greater degree of uncertainty in these total energies. In particular, the energies may be too low whereas for many other states the energies are too high. Theoretical wavelengths for transitions to states where the present calculations have included interactions with only part of the lower-lying Rydberg series can be expected to be too long.

The $2p4p\,{}^4S$ and ${}^4D$ states were both unusual. In the case of the latter, a stationary solution was obtained, though there was substantial mixing of configurations as shown in Table III, where the admixture is referred to simply as $2snd$. For $2p4p\,{}^4S$ the CI-type of calculation described in the previous paragraph produced strong mixing with the $2sns\,{}^4S$ Rydberg series, probably because the oscillations of the ns orbital are more penetrating than those of other nl orbitals. The $2p4p$ configurations lie somewhat lower in the Rydberg series than the $2p4d$ and $2p4f$ configurations and so, in the case of $2p4p\,{}^4S$, the Rydberg series was extended to include configurations up to $2s14s\,{}^4S$. (The energy of the $2p4p\,{}^4S$ configuration state is close to that of $2s12s\,{}^4S$.) All eigenvalues and eigenvectors were computed. The $2p4p\,{}^4S$ configuration was found to be spread over several states. In none of the states was it the dominant component. Its maximum contribution to the composition of a wave function was 33%. For this reason, no energy is reported in Table II.

Further comments pertaining to the $2p4s$ and $2p4d\,{}^4P^o$ states are necessary. The Hartree-Fock energy for $2p4s\,{}^4P^o$ is close to that of $2s7p\,{}^4P^o$ and so $2p4s$ cannot be viewed as a high-lying perturber. On the other hand, $2p4d\,{}^4P^o$ is near the $1s2s\,{}^3S$ ionization limit. In both these cases we have, in effect, *three* interacting Rydberg series: $2snp$, $2pns$, and $2pnd$. The $2p4s\,{}^4P^o$ state is the first in which each of these series have lower members. For the $2p4s\,{}^4P^o$ state, a strict upper-bound energy was obtained by including all lower-lying members in the expansion. Hartree-Fock functions were obtained for $2p_2 4s_1$ and $2p_1 3d_1$. Then, with $2p_2$, $4s_1$, and

$3d_1$ fixed, an MCHF calculation was performed including the first six configurations in the expansion listed in Table I. Finally a CI-type calculation was performed including all the configurations listed. Basis functions were obtained from Hartree-Fock—type calculations. For example, a $3s_1$ orbital was obtained from a calculation for $2p_2 3s_1$ in which $2p_2$ was fixed and $3s_1$ required to be orthogonal to $4s_1$. The calculation for $2p4d\,^4P^o$ was similar to that for other high-lying members of a Rydberg series (where only some of the lower terms are included) except that now terms from both the $2snp$ and $2pns$ Rydberg series were included in the final calculation and the $4d$ orbital was not varied.

In summary, $2pnl$ quartet states, $l \geq 1$, are high-lying perturbers in a Rydberg series. Table II shows that $2p4f\,^4D$ and ^4G are very near the $1s2s\,^3S$ ionization limit. (The energy was computed with the use of an MCHF expansion over the states $\{1s2s_1, 2s_2 3s_2, 2p_1 3p_1,\}\,^3S$, consistent with other expansions.) In order to get a better understanding of the effect of interactions with the remaining $2snl$ or $2s\epsilon l$ channel, further calculations were performed for $2p4d\,^4F^o$. Correlation in the first calculation (neglecting the Rydberg series) reduced the Hartree-Fock energy to a level between the Hartree-Fock energy of $1s2s12f$ and $1s2s13f$. Extending the fixed basis for the second calculation (for which the energy is denoted by footnote e in Table II) produced a wave function for which the $2p4d$ composition was only 30%. At the same time it was noticed that use of the $1s$ orbital from the first calculation had shifted the Hartree-Fock energies of the Rydberg series upward. This was not important for lower-lying members but critically affected the interaction with the nearest members of the series. A new basis was generated through the use of $1s$ and $2s$ orbitals from the $1s2s\,^3S$ ionization limit. Then an MCHF calculation was performed with $13f, 4d_1, 2p_1, 3d_1, 3p_1$ allowed to vary. The final energy was close to the one with the previous basis but the $2p4d\,^4F$ composition had increased to 55%. Clearly, the wave functions are sensitive to small effects in such cases whereas the energy is more stable. Also evident in Table II is the fact that the lower-lying members alone will raise the energy, higher-members together with the continuum lower the energy. In the present case, the final energy is even slightly lower than that of the first calculation but no general conclusion should be drawn from this observation. The $2p4f\,^4G$ and ^4D states lie higher in the Rydberg series with more members interacting so as to raise the energy. It was noticed that, in comparison with the $2p4d\,^4F^o$-$2s9f\,^4F^o$ interaction, the $2p4f\,^4G$-$2s9g\,^4G$ interaction was of similar magnitude whereas the $2p4f\,^4D$-$2s9d\,^4D$ interaction was smaller by more than an order of magnitude. It seems plausible that the $2p4f\,^4D$ energy may be relatively insensitive to the upper portion of the $\{2snd, 2s\epsilon d\}\,^4D$ channel. The lower members, because of their overlap with the $2p4f$ configuration state, have shifted the energy slightly.

IV. WAVELENGTHS, TRANSITION PROBABILITIES, AND LIFETIMES

In Table IV, wavelengths for transitions (λ_{vac}), length and velocity forms of f values, transition probabilities (in 10^8 sec^{-1}), and lifetimes for the upper state (in nanoseconds) are reported. These are compared with other theory, when available, as well as experiment. Generally, the present wavelengths (computed using $R_{\text{Be}} = 109\,730.6$) are in better agreement with observation than those of Laughlin,[5] not quite as good as those of Galán and Bunge,[1] and considerably better than the values reported by Ali.[13]

Accuracy can also be assessed by comparing the length and velocity forms of the f values. In most cases, when f is not too small (>0.01) the discrepancy between length and velocity forms is less than 10% and often only a few percent.

Of particular interest are transitions to $2pnl$ states where the dominant configurations are perturbers in a Rydberg series. The f values for transitions to these states often also have a larger than usual discrepancy between the length and velocity forms. Table IV includes some results based on calculations neglecting interactions with the series, calculations including interactions with some of the lower-lying members, and calculations including all lower-lying members. Lifetimes for the first two are followed by the footnotes b and a, respectively, whereas those for the third set are considered complete and have no special designation. In all cases where the first two results are present, the effect of interactions with some of the lower-lying members is such as to reduce the wavelength of the transition and to shorten the lifetime. Length and velocity forms usually come into better agreement though the $2p3d\,^4D^o$-$2p4f\,^4D$ and $2p3d\,^4F^o(2)$-$2p4f\,^4F$ transitions are exceptions to this observation. In the case of the $2p3p\,^4D$ and $2s4d\,^4D$ transitions to $2p4d\,^4F^o$ the third set of results could also be completed. Because the total energy decreased with the inclusion of the Rydberg series above the $2p4d\,^4F^o$

TABLE IV. Some MCHF results for Be II compared with experiment and other theory when available.

		Present work					Other theory			Experiment		
Transition		λ(Å)	f_l	f_v	A	τ	λ(Å)	τ	Ref.	λ(Å)	τ	Ref.
$2s2p\,^4P^o$	$2p4p\,^4P$	604.4	0.009	0.009	0.017	4.7						
$2s2p\,^4P^o$	$2p4p\,^4D$	609.6	0.009	0.009	0.010	5.4						
$2s2p\,^4P^o$	$2p3p\,^4P$	713.8	0.013	0.014	0.029	2.70	710.9		9	714.2		3
$2s2p\,^4P^o$	$2s4d\,^4D$	715.5	0.099	0.101	0.077	1.17	717.2	1.16	5	714.6	1.2±0.3	3
$2s2p\,^4P^o$	$2p3p\,^4S$	716.8	0.006	0.006	0.023	3.97	713.9		8	716.4		3
$2s2p\,^4P^o$	$2p3p\,^4D$	736.2	0.036	0.035	0.027	2.79	739.3	2.8	5	736.4	2.7±0.3	4
							738.6		13			
$2s2p\,^4P^o$	$2s4s\,^4S$	755.2	0.015	0.016	0.054	1.4	753.5		8	754.4	1.6±0.2	3
$2p^2\,^4P$	$2p4d\,^4P^o$	796.9	0.042	0.045	0.044	1.8[a]						
$2p^2\,^4P$	$2p4d\,^4D^o$	803.6	0.169	0.171	0.105	0.85	799.9		13	803.1	0.83±0.06	3
$2p^2\,^4P$	$2p4s\,^4P^o$	841.1	0.013	0.016	0.013	3.0						
$2s2p\,^4P^o$	$2s3d\,^4D$	867.9	0.524	0.516	0.278	0.359	869.8	0.359	5	867.1	0.64±0.07	3
$2p^2\,^4P$	$2p3d\,^4P^o$	959.5	0.145	0.149	0.105	0.90	968.2	0.90	5	960.0	0.9±0.1	3
$2p^2\,^4P$	$2p3d\,^4D^o$	981.3	0.620	0.626	0.258	0.378	973.7		13	981.7	0.45±0.03	3
$2s2p\,^4P^o$	$2s3s\,^4S$	1021.5	0.052	0.054	0.099	1.0	1020		8	1020.1		14
$2p^2\,^4P$	$2p3s\,^4P^o$	1154.9	0.123	0.121	0.062	1.5				1155.9		14
$2s3d\,^4D$	$2p4d\,^4F^o$	1955.2	0.006	0.009	0.001	8.0[b]						
		1958.0	0.001	0.001	0.000	12.0						
$2s2p\,^4P^o$	$2p^2\,^4P$	2331	0.257	0.234	0.019	5.27	2318		9	2324.6	3.1±0.2	14
$2s3d\,^4D$	$2s6f\,^4F^o$	2420	0.070	0.071	0.006	12.0						
$2s4f\,^4F^o(1)$	$2p5f\,^4F$	2538	0.014	0.013	0.001	5.7						
$2s3s\,^4S$	$2s4p\,^4P^o$	2562	0.067	0.066	0.002	15.1	2540		8	2562.9	13±2	3
$2p3d\,^4D^o$	$2p6f\,^4F$	2603	0.047	0.047	0.003	11.7						
$2s3d\,^4D$	$2s5f\,^4F^o$	2762	0.157	0.162	0.010	7.3	2783	6.4	5	2764	5.6±0.5	4
$2p3s\,^4P^o$	$2p4p\,^4P$	2782	0.015	0.014	0.001	4.7						
$2p3s\,^4P^o$	$2p4p\,^4D$	2895	0.056	0.050	0.003	5.4						
$2p3d\,^4F^o(2)$	$2p5f\,^4F$	2944	0.022	0.023	0.002	5.7						
$2p3d\,^4D^o$	$2p5f\,^4F$	3035	0.137	0.137	0.007	5.7	3058	6.0	5	3031	6.7±0.5	4
$2p3p\,^4D$	$2p4d\,^4P^o$	3072	0.014	0.014	0.002	1.8[a]						
$2s3d\,^4D$	$2p3d\,^4P^o$	3134	0.042	0.041	0.005	0.90						
$2s3s\,^4S$	$2p3s\,^4P^o$	3165	0.179	0.222	0.004	1.5	3169		8	3180	2.4±0.3	14
$2p3p\,^4D$	$2p4d\,^4D^o$	3173	0.008	0.007	0.001	0.85						
$2s3p\,^4P^o$	$2p3p\,^4P$	3219	0.086	0.092	0.005	2.70				3231	2.7±0.5	3
$2s3p\,^4P^o$	$2s4d\,^4D$	3255	0.181	0.185	0.007	1.17				3240	1.2±0.2	3
$2p3p\,^4D$	$2p4d\,^4F^o$	3275	0.262	0.282	0.012	8.0[b]				3435	4.0±0.4	4
		3259	0.270	0.273	0.012	6.3[a]						
		3284	0.173	0.182	0.008	12.0						
$2s3p\,^4P^o$	$2p3p\,^4S$	3282	0.006	0.005	0.001	3.97	3235		8	3261		3
$2s4f\,^4F^o(1)$	$2p4f\,^4D$	3340	0.018	0.014	0.002	5.1[b]						
		3313	0.035	0.006	0.003	4.2						
$2s4f\,^4F^o(1)$	$2p4f\,^4G$	3362	0.184	0.112	0.008	4.2[b]						
		3318	0.064	0.064	0.003	3.9[a]						
$2s3d\,^4D$	$2p3d\,^4D^o$	3379.4	0.114	0.114	0.007	0.378	3380.6	0.39	1	3379.9	0.39	2
							3379.4	0.38	5	3380.0	0.45±0.05	3
$2s4s\,^4S$	$2p4s\,^4P^o$	3403	0.168	0.150	0.003	3.0						

TABLE IV. (*Continued.*)

Transition		Present work					Other theory			Experiment		
		λ(Å)	f_l	f_v	A	τ	λ(Å)	τ	Ref.	λ(Å)	τ	Ref.
$2s4f\,{}^4F^o(1)$	$2p4f\,{}^4F$	3414	0.156	0.138	0.009	3.28	3405.6	3.3	1	3405.4	3.0±0.4	2
$2p3p\,{}^4S$	$2p4d\,{}^4P^o$	3463	0.207	0.168	0.004	1.8[a]						
$2s4d\,{}^4D$	$2p4d\,{}^4P^o$	3493	0.029	0.025	0.003	1.8[a]						
$2s3d\,{}^4D$	$2p3d\,{}^4F^o(2)$	3499	0.378	0.365	0.015	6.24	3510.8	5.9	1	3510	5.3±0.1	2
							3526.4	6.1	5			
$2s4p\,{}^4P^o$	$2p4p\,{}^4P$	3507	0.046	0.075	0.003	4.7						
$2p3p\,{}^4P$	$2p4d\,{}^4P^o$	3535	0.037	0.036	0.002	1.8[a]						
$2s4d\,{}^4D$	$2p4d\,{}^4D^o$	3625	0.105	0.103	0.005	0.85				3624	0.89±0.08	3
$2p3p\,{}^4P$	$2p4d\,{}^4D^o$	3670	0.260	0.259	0.008	0.85				3636	0.89±0.08	3
$2s4p\,{}^4P^o$	$2p4p\,{}^4D$	3689	0.155	0.103	0.005	5.4						
$2s5g\,{}^4G$	$2p5g\,{}^4G^o$	3716	0.088	0.076	0.004	8.8						
$2s3p\,{}^4P^o$	$2p3p\,{}^4D$	3732	0.308	0.283	0.009	2.79	3776.9	2.8	5	3749	3.1±0.3	4
$2s6f\,{}^4F^o$	$2p6f\,{}^4F$	3748	0.076	0.065	0.004	11.7						
$2s4d\,{}^4D$	$2p4d\,{}^4F^o$	3758	0.004	0.034	0.000	8.0[b]				3995	3.6±0.3	4
		3737	0.056	0.074	0.002	6.3[a]						
		3769	0.014	0.019	0.001	12.0						
$2s5f\,{}^4F^o$	$2p5f\,{}^4F$	3797	0.066	0.060	0.003	5.7	3793.0	6.0	5	3785	6±1	4
$2p3p\,{}^4D$	$2p4s\,{}^4P^o$	3853	0.037	0.035	0.003	3.0						
$2p3d\,{}^4F^o(2)$	$2p4f\,{}^4D$	4082	0.031	0.040	0.002	5.1[b]						
		4041	0.057	0.020	0.003	4.2						
$2p3d\,{}^4F^o(2)$	$2p4f\,{}^4G$	4114	0.507	0.635	0.016	4.2[b]						
		4045	0.696	0.629	0.022	3.9[a]						
$2p3d\,{}^4F^o(2)$	$2p4f\,{}^4F$	4192	0.000	0.000	0.000	3.28						
$2p3d\,{}^4D^o$	$2p4f\,{}^4D$	4258	0.106	0.126	0.004	5.1[b]						
		4213	0.120	0.092	0.005	4.2[a]						
$2s3p\,{}^4P^o$	$2s4s\,{}^4S$	4279	0.146	0.156	0.016	1.4	4248		8	4252.1		2
$2s3d\,{}^4D$	$2s4f\,{}^4F^o(1)$	4322	0.378	0.373	0.010	10.3	4330.1	10.0	1	4329.55	11.7±0.2	2
$2p3d\,{}^4D^o$	$2p4f\,{}^4F$	4378	0.864	0.864	0.022	3.28	4371.8	3.3	1	4371.1		2
$2s4d\,{}^4D$	$2p4s\,{}^4P^o$	4539	0.017	0.021	0.001	3.0						
$2s3d\,{}^4D$	$2s4p\,{}^4P^o$	4608	0.056	0.057	0.003	15.1				4596	12.0	3
$2p3p\,{}^4P$	$2p4s\,{}^4P^o$	4611	0.191	0.180	0.006	3.0						
$2p3d\,{}^4P^o$	$2p4f\,{}^4D$	4724	0.683	0.803	0.012	5.1[b]						
		4669	0.721	0.765	0.013	4.2[a]						
$2p3p\,{}^4D$	$2s6f\,{}^4F^o$	4828	0.002	0.002	0.000	12.0						
$2p3d\,{}^4D^o$	$2p4p\,{}^4P$	4848	0.029	0.028	0.001	4.7						
$2p3d\,{}^4F^o(2)$	$2p4p\,{}^4D$	4942	0.010	0.012	0.000	5.4						
$2p3d\,{}^4D^o$	$2p4p\,{}^4D$	5202	0.012	0.013	0.000	5.4						
$2p3d\,{}^4P^o$	$2p4p\,{}^4D$	5915	0.013	0.011	0.000	5.4						
$2s4d\,{}^4D$	$2s6f\,{}^4F^o$	5957	0.189	0.167	0.003	12.0						
$2p4d\,{}^4F^o$	$2p6f\,{}^4F$	5985	0.010	0.012	0.000	12.0						
$2s5f\,{}^4F^o$	$2p4f\,{}^4G$	5995	0.030	0.042	0.000	4.2[b]						
$2s5f\,{}^4F^o$	$2p4f\,{}^4F$	6161	0.002	0.005	0.000	3.28						
$2p4d\,{}^4D^o$	$2p6f\,{}^4F$	6298	0.021	0.022	0.000	11.7						
$2p3p\,{}^4D$	$2s5f\,{}^4F^o$	6415	0.005	0.004	0.000	7.3						
$2s4f\,{}^4F^o(1)$	$2s5g\,{}^4G$	7914	0.599	0.568	0.005	14.0						

TABLE IV. (*Continued.*)

Transition		Present work					Other theory			Experiment		
		λ(Å)	f_l	f_v	A	τ	λ(Å)	τ	Ref.	λ(Å)	τ	Ref.
$2s4d\,^4D$	$2s5f\,^4F^o$	8574	0.594	0.508	0.004	7.3						
$2p4d\,^4F^o$	$2p5f\,^4F$	8776	0.051	0.057	0.000	5.7[b]						
$2p3p\,^4D$	$2p3d\,^4P^o$	8854	0.022	0.008	0.000	0.90						
$2s3s\,^4S$	$2s3p\,^4P^o$	8972	0.683	0.701	0.002	19.1	9010		8			
$2p3s\,^4P^o$	$2p3p\,^4P$	9427	0.313	0.331	0.002	2.70						
$2p4d\,^4D^o$	$2p5f\,^4F$	9605	0.744	0.744	0.004	5.7						
$2p3s\,^4P^o$	$2s4d\,^4D$	9741	0.020	0.019	0.000	1.17						
$2p4f\,^4F$	$2p5g\,^4G^o$	9754	1.230	1.232	0.007	8.8						
$2p3s\,^4P^o$	$2p3p\,^4S$	9981	0.066	0.059	0.001	3.97	9564		8			
$2p4f\,^4G$	$2p5g\,^4G^o$	10202	0.065	0.080	0.000	8.8[b]						
$2p3p\,^4D$	$2p3d\,^4D^o$	11140	0.044	0.063	0.000	0.378						
$2p3p\,^4D$	$2p3d\,^4F^o(2)$	12554	0.358	0.338	0.001	6.24						
$2s4d\,^4D$	$2p3d\,^4P^o$	13569	0.073	0.063	0.000	0.9						
$2p3d\,^4F(2)$	$2s5g\,^4G$	13896	0.774	0.723	0.002	14.						
$2p3s\,^4P^o$	$2p3p\,^4D$	15770	0.239	0.172	0.000	2.79						
$2s3p\,^4P^o$	$2s3d\,^4D$	16177	0.213	0.211	0.000	0.36						
$2p3p\,^4P$	$2p3d\,^4D^o$	21230	0.170	0.184	0.000	0.378						
$2s4s\,^4S$	$2s4p\,^4P^o$	22148	1.072	1.171	0.000	15.						
$2s4d\,^4D$	$2p3d\,^4F^o(2)$	24751	0.277	0.278	0.000	6.24						
$2p4s\,^4P^o$	$2p4p\,^4P$	27394	0.381	0.378	0.000	4.7						
$2s4p\,^4P^o$	$2s4d\,^4D$	36274	0.482	0.532	0.000	1.17						
$2s4p\,^4P^o$	$2p3p\,^4S$	38636	0.025	0.035	0.000	3.97						

[a] Including interactions with some of the lower-lying members of a Rydberg series.
[b] Omitting interactions with a $2snl$ Rydberg series.

configuration, as explained in Sec. III, the wavelength has again increased. More important is the fact that the dilution of the wave function with the Rydberg series has increased the lifetime, but since the mixing is sensitive to the details of the calculation, the lifetimes are highly uncertain.

The wavelengths reported in Table IV are based on energies corrected for relativistic shift effects. In Table V some present results are evaluated by comparing nonrelativistic transition energies (ΔE_{NR}) and corrections to these energies with similar quantities reported by Galán and Bunge. In the case of ΔE_{NR}, the Galán and Bunge results are essentially exact. Their corrections to this quantity

TABLE V. Comparison of present nonrelativistic energy differences (in cm^{-1}) and corrections to these differences compared with those reported by Galán and Bunge (Ref. 1). Corrections in parentheses reflect the effect of mass polarization (see text).

Transition	ΔE_{NR}	Corrections
$2s3d\,^4D$-$2s4f\,^4F^o(1)$	23119.0	20.6(16.2)
	23072.8[a]	14.7[a]
$2s3d\,^4D$-$2p3d\,^4F^o(2)$	28560.2	18.6(14.6)
	28461.6[a]	14.3[a]
$2s3d\,^4D$-$2p3d\,^4D^o$	29545.7	43.9(34.5)
	29535.8[a]	35.9[a]

[a] Galán and Bunge (Ref. 1).

include not only relativistic effects but also radiative and mass polarization corrections. For the $1s\,2s\,{}^3S$-$1s\,2p\,{}^3P^o$ energy difference in Be III they estimate the corrections to the nonrelativistic value to be 39.6 cm^{-1}. According to Accad, Pekeris, and Schiff,[15] the relativistic correction is 50.39 cm^{-1} and the mass-polarization correction is -9.81 cm^{-1} for a total correction of 40.6 cm^{-1}. Presumably the remaining difference is the radiative correction. Galán and Bunge assume transferability of these corrections to three-electron systems. Clearly the radiative and mass-polarization effects are smaller than the relativistic correction and cancel some of the latter. If the present relativistic corrections are multiplied by a similar factor the values included in parentheses in Table V are obtained. We conclude that the most important correction neglected is the mass-polarization correction, that the relativistic correction is reliable, and that the limiting factor on accuracy here is still the nonrelativistic calculation.

V. INTERPRETATION OF THE DATA

It is not the intention here to dwell on earlier assignments that have been reclassified in view of subsequent theoretical calculations. Indeed, in Table IV, where experimental results are also reported, only the more recent interpretations are included. On the whole, the present results support predictions made on the basis of other theoretical calculations. The present energy for $2p\,3p\,{}^4S$, lower than the one obtained by the Larsson *et al.*,[8] predicts a wavelength of 716.8 Å for the $2s\,2p\,{}^4P^o$-$2p\,3p\,{}^4S^o$ transition and supports the assignment of the line at 716.4 Å to this transition. The value of Larsson *et al.* of 713.9 Å left the assignment somewhat in doubt particularly in view of the line at 714.2 Å, assigned correctly to the $2s\,2p\,{}^4P^o$-$2p\,3p\,{}^4P$ transition but without the support of theoretical calculations.

In comparing present results with experimental identifications where no other theoretical calculations have been reported, two cases stand out clearly. These are the $2p\,3p\,{}^4D$-$2p\,4d\,{}^4F^o$ and $2s\,4d\,{}^4D$-$2p\,4d\,{}^4F^o$ transitions assigned recently by Bentzen *et al.*[4] Before discussing these assignments, some comments concerning the accuracy of wavelengths (as distinct from transition energies) is in order.

Theoretical wavelength accuracy depends on several factors. Generally, the energies of states lowest of their symmetry are determined most accurately with the computed energy a strict upper bound. The accuracy decreases for excited states when lower-lying states interact with a perturber so as to raise the energy of a state. The errors are expected to be greatest for the high-lying perturbers of a Rydberg series. In spite of the varying accuracy, the total energies, and consequently also the transition energies, are uncertain in an absolute error sense. When comparing the total energies of Table II with those reported by Galán and Bunge, differences of 0.0003 to 0.0008 a.u. were noted. In each case the errors were in the same direction. When such energies are differenced, errors of up to 0.0005 a.u. or 110 cm^{-1} are produced. The errors for more highly excited states may be somewhat larger, but unless there is an interaction with a Rydberg series, the error is not expected to be more than 200^{-1}. Clearly then, on a relative scale, the error in λ will be smaller when ΔE is large (λ small) and larger when ΔE is small (λ large). If we accept an uncertainty of 200 cm^{-1} in ΔE, this would lead to $\lambda = 3000 \pm 18$ Å and $\lambda = 4000 \pm 32$ Å. For all transitions, except the two mentioned earlier, namely, $2p\,3p\,{}^4D$-$2p\,4d\,{}^4F^o$ and $2s\,4d\,{}^4D$-$2p\,4d\,{}^4F^o$, the experimental wavelengths fall within these error limits.

The search for an alternative assignment for the observed lines at 3435 and 3995 Å, in better agreement with theory, motivated many of the calculations reported in Table IV. The wavelength in Table IV closest to the 3435 Å value is 3463 Å for the $2p\,3p\,{}^4S$-$2p\,4d\,{}^4P^o$ transition. Of the two energies involved, that of $2p\,4d\,{}^4P^o$ has the greatest uncertainty associated with it. The neglected interaction with the upper portion of the $2snp\,{}^4P^o$ Rydberg series and the $2s\epsilon p$ continuum could raise the energy further, decreasing the wavelength and bringing it in better agreement with that of the observed. The predicted lifetime for $2p\,4d\,{}^4P^o$ of 1.8 ns is not in good agreement with the measured lifetime of 4.0 ± 0.4 ns. As was shown in the case of the $2p\,4d\,{}^4F^o$ state, the dilution of the wave function by the Rydberg series could increase the lifetime by a factor of 2.

The results of Table IV suggest a possible assignment of the $2p\,3d\,{}^4F^o(2)$-$2p\,4f\,{}^4G$ transition to the 3995-Å line. There is a larger than usual discrepancy between the theoretical and observed wavelength but in this case a plausible explanation exists. In Table II it is shown that our energy for $2p\,3d\,{}^4F^o(2)$ is too high and that the inclusion of interactions with the lower-lying members of the Rydberg series, $2sng$, $n = 5$ to 14, has raised the energy of the $2p\,4f\,{}^4G$ state. The remaining interactions could raise the energy further. Thus the errors in the total energies—too high for the lower state and too low for the upper—do not cancel when transition energies are computed and lead to a theoretical wavelength that is too long. Finally, the f value for the transition is large, indicating the possibility of a fairly intense line. Length and velocity forms of the f value are in good agreement when some interactions with the Rydberg series are included, increasing one's confidence in the result. The theoretical lifetime of 3.9 ns in this case is in excellent agreement with the measured lifetime of 3.6 ± 0.3 ns. But since the calculation is incomplete in that not all the Rydberg series has been included, the theoretical lifetime cannot be considered reliable.

Another transition for which the theoretical calculation predicts a large f value and transition probability is the $2p\,3d\,{}^4P^o$-$2p\,4f\,{}^4D$ transition. Again, the upper state is a high-lying perturber but in this case the interaction with $2snd$ is smaller and the predicted wavelengths can be expected to be more accurate. Martinson[16] has reported that their group has observed two lines, one with $\lambda_{\text{air}} = 4039.38 \pm 0.88$ Å and the other with $\lambda_{\text{air}} = 4663.74 \pm 0.60$ Å. Table IV suggests the former might be the $2p\,3d\,{}^4F^o(2)$-$2p\,4f\,{}^4D$ transition. If this is the case, the observed wavelength data predicts a separation of 3313 cm^{-1} for the $2p\,3d\,{}^4F^o(2)$ and $2p\,3d\,{}^4P$ states. The present theoretical energy separation for these two states is 3314 cm^{-1}.

Table IV also includes data for $2p\,4p\,{}^4P$ and ${}^4D$ states required for the analysis of experimental data. Interpretations based on these calculations are presented in an accompanying paper.[17]

VI. CONCLUSIONS

In effect, the present calculations have attempted to analyze a spectrum. When such a large number of calculations are involved, it becomes costly to perform calculations for each state to spectroscopic accuracy as defined by Galán and Bunge. The results reported here show that when transition energies, f values, and lifetimes are available, lesser accuracy can suffice. For example, on the basis of the f values the relatively strong observed line at 3510 Å with a lifetime of 5.3 ns would be assigned the $2s\,3d\,{}^4D$-$2p\,3d\,{}^4F^o(2)$ transition (which the more accurate calculations by Galán and Bunge have verified) rather than the $2s\,4p\,{}^4P^o$-$2p\,4p\,{}^4P$ transition. In Table IV the latter has a closer theoretical wavelength, but the f value is almost an order of magnitude smaller (the length form being the more reliable estimate) indicating a much weaker line.

Many of the results reported here for excited states were stationary solutions for which the upper-bound property is not assured, *a priori.* The energy may, however, still be an upper bound (see the discussion in Ref. 11, for example). The energies obtained from a variational procedure (which includes a variation of the orbital basis) were generally in better agreement with observation than when some of the orbitals were fixed to assure stability or to assure an energy upper bound. In all cases, the stationary results have produced transition wavelengths in better agreement with observation than those of Larsson *et al.*

The present MCHF calculations have not been able to determine reliable wave functions for high-lying perturbers. Some of these are near the ionization limit. It would be interesting to compare the present predictions with those of some other method, such as the multichannel quantum defect method. A study of B III** would also clarify the situation. In the B III** spectrum the $2p\,4l$ states would no longer be located so near the ionization limit and MCHF calculations could be performed more reliably.

The interpretation of the data, as presented in Sec. V, assumed that the unidentified lines mentioned were part of the quartet system. It is conceivable that some or all of the lines belong to the doublet system for which no theoretical calculations have been reported to date.

It is encouraging to note that, in this case, theoretical and beam-foil lifetimes generally are in good agreement. The calculations reported here could not have been performed without programs for evaluating angular integrals given a nonorthogonal orbital basis.[12] The ability to represent a correlated wave function with a relatively small number of configuration states relies on the use of sets of orthogonal orbitals rather than a single orthogonal basis. Furthermore, as in a HF calculation, the orbital bases for the initial and final states are not the same. The problem of evaluating transition matrix elements between such states is equivalent to the problem of evaluating matrix elements under the assumption of nonorthogonal orbitals.

Note added in proof. Laughlin (private communication) has found $2p\,4d\,{}^4F^o$ to lie between $2s\,13f$ and $2s\,14f$. The neglect, in the present calculations, of $1s2s\,{}^3S$ correlation for members of the Rydberg series may account for this discrepancy.

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