PHYSICAL REVIEW A VOLUME 48, NUMBER 3 SEPTEMBER 1993

Energies, fine structures, and isotope shifts of the $1s^2 2snl$ excited states of the beryllium atom

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(Received 3 March 1993)

The energies and wave functions of the $1s^2 2snl$ states of beryllium are calculated with a full-core plus correlation method. Eight excited states ($2p\,^{1,3}P^o$, $3s\,^{1,3}S$, $3p\,^{1,3}P^o$, and $3d\,^{1,3}D$) are studied. A restricted variational method is used to extrapolate a better nonrelativistic energy. The relativistic corrections are calculated with first-order perturbation theory. The calculated excitation energies (relative to the ground state) are compared with experiment. For the $2p\,^3P^o$, $3s\,^{1,3}S$, $3p\,^3P^o$, and $3d\,^3D$ states, the predicted energies agree with experiment to about 1 cm^{-1}. However, the discrepancies are larger for $2p\,^1P^o$, $3p\,^1P^o$, and $3d\,^1D$. The relativistic corrections are found to be critically important in these comparisons. The predicted fine-structure splittings for $2p\,^3P^o_{2,1,0}$ are 2.360 and 0.637 cm^{-1}. They agree well with the 2.35 and 0.64 cm^{-1} in the experiment. The predicted ^{10}Be–^{9}Be $2s\,^1S$–$3d\,^1D$ isotope shift is 14.08 GHz. This also agrees with the 14.05(4) GHz in the experiment. The lifetime of the $1s^2 2s2p\,^3P^o_1$ is calculated using the intermediate-coupling scheme.

PACS number(s): 31.20.Di, 31.20.Tz, 31.30.Jv, 31.50.+w

I. INTRODUCTION

Extensive theoretical researches have been done on the excited states of beryllium in the literature [1–16]. Most of the work studied the oscillator strengths and lifetimes of these four-electron systems and comparisons have been made with experiment [17–20]. Although the transition energies between these states are given in most cases, only a few have predicted the nonrelativistic energy [21, 22]. Very few have studied the relativistic effects of these excited states [23]. By contrast, there have been numerous studies on the nonrelativistic energy and relativistic effect of the Be I ground state in the literature [24]. The lack of attempts to calculate an accurate energy for Be I excited states could be an indication of the challenge facing such a study.

The energy and some of the fine structures of the Be system have been accurately determined over 30 years ago [25]. More recently, the isotope shifts of the ^{10}Be–^{9}Be have been measured using two-photon resonance ionization mass spectroscopy [26]. The precision of the shifts has been given to within ±40 MHz. To our knowledge, no theoretical study has successfully compared with these experimental results.

Recently, a full-core plus correlation method (FCPC) has been carried out to study the ground state of the Be-like isoelectronic sequence [27]. The ionization potentials (IP) of these ground states are calculated from $Z = 4$ to 25. They agree to the highly precise experimental data. For example, the predicted IP for Be I, C III, N IV, O V, and F VI are 75 192.17, 386 240.0, 624 863.8, 918 657.2, and 1 267 606.7 cm^{-1}. They agree with the experimental results 75 192.07(10) [25], 386 240(1) [28], 624 866(3) [29], 918 657(4) [30], and 1 267 606(2) cm^{-1} [31], respectively. The calculated mass polarization effect for the Be I ground state also agrees with that of Wen *et al.* [26]. This shows that substantial progress has been made on the calculation of ground-state correlation energy for four-electron systems. It would be interesting to find out whether the FCPC method can also be successful for Be-like excited states. Therefore, to carry out such a study on Be I excited systems, where highly precise experimental data are available, we will answer this question and illuminate the challenge ahead.

Among the four-electron excited systems, the low-lying excited states are probably the most challenging from a theoretical point of view since correlation effects are strong in these systems. In this work, we carry out a FCPC calculation for all the Be I $1s^2 2snl$ states for $n \leq 3$. There are eight such excited states. We have not attempted to calculate all the low-lying excited states since each of these calculations is quite complicated. In the experiment of Johansson [25], some of the fine-structure splittings are not resolved. We will calculate the fine-structure splittings of the triplet systems to compare with experiment. This will give us a better understanding of the experimental data.

II. THEORY

The Hamiltonian and perturbation operators used in this work are the same as those of Chung, Zhu, and Wang [27]. They will not be repeated here. The main difference in terms of the numerical method is that we used a restricted variational method [32] in addition to the conventional Rayleigh-Ritz variation method. The procedure is similar to that of Chang [33], except that the basis functions are not orthogonal and they may "oversaturate" the functional space. Variation is carried out by optimizing the nonlinear parameters in the oversaturated wave function. The variation is restricted in the sense that the major part of the wave function is used as a single term and the parameters in this part no longer vary. In the work of Chung and Zhu [32], it has been shown that this method avoids numerical instabilities which normally occurs due to linear dependence.

To implement this restricted variation method in FCPC, we first write a "basic function" for the four-electron system:

$$\Psi_b(1,2,3,4) = \Psi_0(1,2,3,4) + \Psi_1(1,2,3,4) \qquad (1)$$

where

$$\Psi_0(1,2,3,4) = A\Phi_{1s1s}(1,2)\Phi_{2snl}(3,4) \qquad (2)$$

and

$$\Psi_1(1,2,3,4) = A\sum_i C_i\Phi_{n(i),l(i)}(1,2,3,4)\ . \qquad (3)$$

A is the antisymmetrizaton operator and C_i are the linear parameters. $\Phi_{1s1s}(1,2)$ is the predetermined $1s1s$-core wave function. It is the same as that given by Chung, Zhu, and Wang [27]. $\Phi_{2snl}(3,4)$ represents the wave function of the two outer electrons. Similar to Ref. [27], only two angular components are included in this part of the wave function. For D states, the angular components (l_3, l_4) are (0,2) and (1,1). They are (0,0) and (1,1) for S states and (0,1) and (1,2) for P states. Most of the other correlation effects are included in Ψ_1, which accounts for the intershell as well as the intrashell correlations. In this work, Ψ_1 contains about 950 terms of basis functions. These basis functions, $\Phi_{n(i),l(i)}(1,2,3,4)$, are the product of Slater orbitals with proper angular-spin functions. They are similar to those of Ref. [27]. We try to include in Ψ_1 those basis functions with significant energy contribution. The sum of Ψ_0 and Ψ_1 gives the "basic wave function" of the four-electron system. The angular components of Ψ_1 can be represented by

$$l(i) = [(l_1, l_2)l_{12}, l_3]l_{123}, l_4 \qquad (4)$$

with the understanding that l_{123} and l_4 couple into L, the total orbital angular momentum. For the eight excited states considered in this work, four are singlets and four are triplets. The singlet spin-wave functions are the same as in Ref. [27]. The triplet spin functions are

$$\chi_1 = [(s_1, s_2)0, s_3]1/2, s_4\ , \qquad (5)$$

$$\chi_2 = [(s_1, s_2)1, s_3]1/2, s_4\ , \qquad (6)$$

and

$$\chi_3 = [(s_1, s_2)1, s_3]3/2, s_4\ . \qquad (7)$$

For the radial basis functions of each angular-spin component, a set of nonlinear parameters is chosen. These parameters are determined in the energy optimization process. For each set of l_1, l_2, l_3, and l_4, we try all possible $l(i)$ and χ, and keep the ones which make significant contribution to the energy in Ψ_1.

For convenience of discussion, we will group the angular-spin components into different orthogonal groups. For example, $[l_1l_2l_3l_4]$ represents the set of all possible $l(i)$ and χ_i which has angular momenta l_1, l_2, l_3, and l_4.

Using the Rayleigh-Ritz variational method, we determine the basic wave function Ψ_b and the corresponding eigenvalue E_b. We then expand the total wave function as

$$\Psi(1,2,3,4) = D_0\Psi_b(1,2,3,4) + \Psi_2(1,2,3,4) \qquad (8)$$

where

$$\Psi_2(1,2,3,4) = A\sum_{i=1}^{I} D_i\psi_{n(i),l(i)}(1,2,3,4)\ . \qquad (9)$$

Ψ_2 is a function to saturate the functional space. It takes essentially the same form as the Ψ_1 in Eq. (3). D_i's are the linear parameters. Ψ_2 may have considerable overlap with the basis functions in Ψ_1. Note that Ψ_b is used as a single term in Ψ. Hence the overlap between the basis functions in Ψ_2 and Ψ_1 does not cause any numerical instability [32]. The (1,1) matrix element of the secular equation constructed from Eq. (8) is $E_b - \lambda$ where λ is the eigenvalue to be solved. In practice, we will break up Ψ_2 into many parts. A secular equation will be constructed for each part. They will be calculated individually. Each of the nonlinear parameters in the basis functions of Ψ_2 is optimized in the restricted variational calculation.

The relativistic and mass polarization perturbation operators are the same as those in Chung, Zhu, and Wang [27]. The explicit expressions will not be repeated. We will use the same notation in this work, i.e., H_1 is the mass correction to kinetic energy, H_2 is the Darwin term, H_3 is the electron-electron contact term, H_4 is the mass polarization, and H_5 is the orbit-orbit interaction. The corrections from H_1, H_2, H_3, and H_5 are all calculated from first-order perturbation theory. Since H_4 is a kinematic effect from the coordinate transformation, we calculate this perturbation to infinite order in this work. This mass polarization effect is very small. The result does not differ appreciably from that of first-order perturbation theory.

The contributions from the QED and the higher-order relativistic effects are calculated using a method described by Chung, Zhu, and Wang [27]. We only consider the QED effect of the two outer electrons. Effective nuclear charges are used in the hydrogenic QED formula in Drake [34]. These effective charges are determined by considering the $2s$ electron in the field of Be^{2+} and the nl electron in the field of Be^+ using the same method as in Ref. [27]. The explicit formula for the s electron is the same as in this reference. For other nl electrons, it is [34]

$$\Delta E_{\mathrm{QED}}(n,l,j) = 4Z_{\mathrm{eff}}^4\alpha^3\left\{\frac{3c_{l,j}}{8(2l+1)} - \ln K(n,l) + (Z_{\mathrm{eff}}\alpha)^2\ln(Z_{\mathrm{eff}}\alpha)^{-2}\left[\left(1-\frac{1}{n^2}\right)\left(\frac{1}{10}+\frac{1}{4}\delta_{j,1/2}\right)\delta_{l,1} + \frac{8\left(3-\frac{l(l+1)}{n^2}\right)}{(2l-1)(2l)(2l+1)(2l+2)(2l+3)}\right] + \frac{3\alpha}{4\pi}(-0.3285)c_{l,j}\Big/(2l+1)\right\}\Big/3\pi n^3 \tag{10}$$

where

$$c_{l,j} = \begin{cases} l/(l+1) & \text{for } j = l+1/2 \\ -1/l & \text{for } j = l-1/2. \end{cases} \tag{11}$$

The values of ln $K(n,l)$ are taken from Drake and Swainson [35]. In this work, the wave function of good quantum numbers (L,S,J,J_z) is expanded in terms of the products of the angular-spin functions of $1s^22s$ and the nl electron. The QED contributions are evaluated accordingly. For beryllium, these QED effects are very small. The higher-order relativistic effect for beryllium is negligible.

For the fine structure, the perturbation operators are

$$H_{\mathrm{so}} = \frac{Z}{2c^2}\sum_{i=1}^{4}\frac{\boldsymbol{l}_i\cdot\mathbf{s}_i}{r_i^3} \qquad \text{(spin orbit)}, \tag{12}$$

$$H_{\mathrm{soo}} = -\frac{1}{2c^2}\sum_{\substack{i,j=1\\ i\neq j}}^{4}\left[\frac{1}{r_{ij}^3}(\mathbf{r}_i-\mathbf{r}_j)\times\mathbf{p}_i\right]\cdot(\mathbf{s}_i+2\mathbf{s}_j) \qquad \text{(spin other orbit)}, \tag{13}$$

and

$$H_{\mathrm{ss}} = \frac{1}{c^2}\sum_{\substack{i,j=1\\ j>i}}^{4}\frac{1}{r_{ij}^3}\left[\mathbf{s}_i\cdot\mathbf{s}_j - \frac{3(\mathbf{s}_i\cdot\mathbf{r}_{ij})(\mathbf{s}_j\cdot\mathbf{r}_{ij})}{r_{ij}^2}\right] . \qquad \text{(spin-spin)}. \tag{14}$$

These perturbations are calculated using first-order perturbation theory.

III. COMPUTATION OF NONRELATIVISTIC ENERGY

As in Ref. [27], we first calculated a basic wave function Ψ_b for each of the eight excited states $1s^22snl\,^{2S+1}L$ where the $nl^{2S+1}L$'s are $2p\,^{1,3}P^o$, $3s\,^{1,3}S$, $3p\,^{1,3}P^o$, and $3d\,^{1,3}D$. These wave functions contain two parts. Ψ_0 is the part with the $1s1s$ core [see Eq. (2)]. The Φ_{2snl} in this part has two angular components. The number of terms in Φ_{2snl} ranges from 45 to 49. The second part is represented by Ψ_1, which represents other correlation effects. The number of terms ranges from 836 to 1038. The energy obtained from Ψ_0 and Ψ_1 is given in Tables

TABLE I. Nonrelativistic energy $(-E)$ of the $1s^22snl$ states of Be I [see Eqs. (1) and (8)].

State	From Ψ_0 (a.u.)	From Ψ_1 [a] (μa.u.)	$E_b(\Psi_0+\Psi_1)$ (a.u.)	High l[b] (μa.u.)	From Ψ_2 [c] (μa.u.)	Total E_{nonrel}[d] (a.u.)	Others (a.u.)
$3s\,^1S$	14.414 519 05	3 438.22	14.417 957 27	12.06	37.69	14.418 237 12	14.370 51 [e]
$3s\,^3S$	14.426 290 63	3 507.91	14.429 798 54	9.94	25.82	14.430 064 40	14.382 3[f]
$2p\,^1P$	14.466 686 53	6 323.12	14.473 009 65	62.64	132.52	14.473 434 91	14.423 55[e]
$3p\,^1P$	14.388 465 86	4 322.42	14.392 788 28	19.65	75.30	14.393 113 33	14.344 56[e]
$2p\,^3P$	14.562 231 00	4 682.79	14.566 913 79	14.92	79.50	14.567 238 30	14.518 44[e] 14.518 4[f]
$3p\,^3P$	14.395 099 06	3 547.73	14.398 646 79	10.20	73.03	14.398 960 12	14.351 06[e] 14.351 0[f]
$3d\,^1D$	14.368 337 21	5 105.20	14.373 442 41	18.31	99.65	14.373 790 48	14.325 76[g]
$3d\,^3D$	14.379 559 32	4 796.98	14.384 356 30	8.89	27.35	14.384 622 60	14.336 9[f]

[a] See Table II.

[b] See Table III.

[c] See Table IV.

[d] A correction of 230.1 μa.u. due to the $1s1s$-core deficiency is included in the total energy of each state.

[e] Weiss [22].

[f] Hibbert [21].

[g] Wen *et al.* [26].

TABLE II. Be I $1s^22snl$ nonrelativistic energy contributions (in μa.u.) from Ψ_1. See Eq. (3). L is the angular component. $[l_1l_2l_3l_4]$ represent the combined contribution from different angular-spin couplings of l_1, l_2, l_3, and l_4.

	P states					*S* states			*D* states	
L	$2p\,^1P$	$3p\,^1P$	$2p\,^3P$	$3p\,^3P$	L	$3s\,^1S$	$3s\,^3S$	L	$3d\,^1D$	$3d\,^3D$
[0001]	1401.11	929.89	922.22	472.87	[0000]	272.71	296.19	[0002]	245.56	285.02
[0012]	787.28	393.53	1427.96	197.72	[0011]	2558.66	2746.61	[0013]	641.12	1431.81
[0023]	1106.97	240.63	302.45	53.29	[0022]	383.54	307.71	[0024]	48.89	34.78
[0034]	273.39	57.62	52.18	6.48	[0033]	72.23	60.65	[0035]	9.85	4.67
[0045]	90.84	19.39	11.06		[0044]	21.67	19.27	[0046]		1.09
[0056]	38.99	7.66	1.84		[0055]	8.46	6.71	[0112]	2632.76	2565.50
[0067]	19.68	3.90	.59		[0066]	4.01	3.34	[0231]	50.22	11.70
[0111]	2222.19	2356.97	1670.42	2506.88	[0112]	98.58	61.21	[0341]	5.66	
[0122]	284.73	247.55	230.42	244.50	[0123]	9.06	4.06	[0222]	181.57	220.37
[3301]	38.79	39.23	38.62	47.45	[0134]	1.78	.64	[0332]	36.63	46.12
[4401]	12.46	12.98	11.01	12.92	[0145]	.48		[0442]	11.81	14.48
[5501]	3.62	3.18	2.90	5.62	[1111]	.26		[0552]		4.74
[6601]	1.75	1.46	1.34		[1122]	5.69	1.52	[0662]		2.21
[0113]	24.18	5.78	7.40		[1133]	.42		[0011]	446.55	16.06
[0124]		.18			[2222]	.67		[0022]	643.38	6.07
[1123]	15.02	2.47	2.38					[0033]	40.32	
[1134]	2.12							[0044]	8.09	
								[1113]	63.84	119.31
								[2213]	8.52	16.43
								[3313]		4.11
								[4413]		1.43
								[1122]	30.43	11.08
Total	6323.12	4322.42	4682.79	3547.73		3438.22	3507.91		5105.20	4796.98

TABLE III. Energy contributions ($-\Delta E$) to the Be I $1s^22snl$ states from Ψ_2 using the restricted variational method. L is the angular component. $[l_1l_2l_3l_4]$ represent the combined contribution from different angular-spin combinations of l_1, l_2, l_3, and l_4. (in μa.u.).

	$3s\,^1S$	$3s\,^3S$	$3d\,^1D$		$3d\,^3D$			$2p\,^1P$	$3p\,^1P$	$2p\,^3P$	$3p\,^3P$
L	ΔE	ΔE	L	ΔE	L	ΔE	L		ΔE		
[0000]	3.89	4.85	[0002]	9.51	[0002]	0.89	[0001]	12.25	7.97	9.73	12.16
[0011]	8.42	4.53	[0011]	4.42	[0011]	1.39	[0012]	26.82	15.25	9.04	8.68
[0022]	4.48	3.42	[0022]	2.21	[0013]	2.20	[0023]	11.88	4.71	5.11	1.99
[0033]	4.16	2.70	[0033]	1.42	[0024]	0.73	[0034]	9.46	2.40	5.02	3.14
[0044]	3.26	1.20	[0044]	1.03	[0035]	0.35	[0045]	12.47	2.31	5.31	2.79
[0055]	2.28	1.99	[0055]	3.11	[0046]	0.44	[0056]	7.42	1.99	4.84	1.12
[0066]	1.18	0.94	[0066]	1.46	[0112]	0.99	[0067]	4.00	1.06	2.52	0.49
[0112]	6.63	3.57	[0013]	13.95	[0222]	5.07	[0111]	5.32	5.65	6.90	12.03
[0123]	1.90	1.70	[0024]	4.28	[0332]	2.10	[0122]	11.01	9.40	10.75	7.63
[0134]	0.45	0.92	[0035]	4.31	[0442]	1.95	[0133]	4.15	5.31	3.43	4.54
[0145]	0.37		[0046]	5.70	[0552]	2.57	[0144]	3.05	3.28	4.92	5.68
[0156]	0.42		[0112]	2.56	[0662]	1.29	[0155]	3.13	3.83	3.64	2.47
[1122]	0.25		[0123]	4.60	[0123]	0.68	[0166]	1.53	2.03	1.97	3.94
			[0134]	4.97	[0134]	0.62	[0113]	0.80	0.37	0.21	0.92
			[0145]	3.74	[1113]	3.33	[0124]	1.78	0.29	0.66	0.09
			[0156]	1.53	[2213]	1.38	[0135]	0.43	0.11		
			[0167]	0.70	[4413]	0.05	[0223]	7.75	1.24	1.18	1.09
			[0222]	7.31	[1122]	0.30	[1112]	5.36	7.09	2.38	3.31
			[0332]	3.86	[5513]	0.68	[1123]	0.97	0.60	0.31	0.81
			[0442]	2.24	[6613]	0.33	[1134]	0.91			
			[0552]	5.97			[1222]	0.38	0.40	0.08	0.17
			[0662]	2.76			[2223]	1.67		0.31	
			[1113]	1.72							
			[0057]	2.98							
			[1122][a]	3.32							
Total	37.69	25.82		99.65		27.35		132.52	75.30	79.50	73.03

[a] Include the contributions of [1111], [1133], [2222], and [0114].

I and II.

As discussed in the preceding section, for each set of orbital angular momenta l_1, l_2, l_3, and l_4, there are many ways they may couple into the total orbital and spin angular momentum of interest. We use $[l_1 l_2 l_3 l_4]$ to represent collectively the group of various angular and spin couplings. In Table II, the energy contribution of each group is given to show the correlation effect for each state. The results in this table show that the triplet states appear to converge faster. The groups with higher l's in the triplets contribute less to the binding energy. This may be part of the reason why our results are better for triplets. This is analogous to the configuration-interaction calculation for heliumlike systems; the energies of triplets converge much faster than those of the singlets [36, 37].

In the present work, we find that S states are easier to compute. There are less angular terms which contribute significantly to the energy. By contrast, the most difficult state in terms of precision calculation is the $1s^2 2s3d\,^1D$. This state is a mixture of $2p2p$, $2s3d$, and $2p3p$ [5]. This makes the search of correlation energy very challenging. In the lithiumlike $1s^2 3d$ states, correlation effects are very small. It is relatively easy to obtain an accurate energy for these D states using FCPC method [38]. The Be I $1s^2 2s3d\,^1D$ state is very different.

The correlation energy in Table II is added to the energy from Ψ_0 to give E_b. E_b is an upper bound to the nonrelativistic energy. In Ref. [27], a partial saturation of basis functions method has been used to extrapolate a better nonrelativistic energy for the berylliumlike $1s^2 2s^2$ states. This method is probably still quite effective for the $3s\,^{1,3}S$ states, but it is no longer adquate for the other six excited states considered in this work. To achieve better numerical accuracy and to include more terms into the wave function we use the restricted variation method discussed in Sec. II. We compute the contribution from each $[l_1 l_2 l_3 l_4]$ group, one at a time. Hence the total energy obtained by summing the contributions is no longer an upper bound to the nonrelativistic eigenvalue. Since these groups are orthogonal and the basic wave function is already quite accurate. The error introduced by such a method is probably very small. The possible error in such a procedure is tested in Chung and Zhu [32]. The contribution from each group calculated with this restricted variation method is given in Table III.

A very important part of the FCPC method is the inclusion of the core correction and the extrapolation of the energy contribution from high-l groups [39]. We have used the same Φ_{1s1s} core wave function as in Ref. [27], hence the energy correction is 230.1 μa.u. This energy should be added to the calculated E_b. The extrapolation

TABLE IV. Extrapolation of $1s^2 2snl$ energies from higher l components (in μa.u.).

L	ΔE	Ratio[a]	ΔE	Ratio[a]	L	ΔE	Ratio[a]		ΔE	Ratio[a]
	$2p\,^1P$		$3p\,^1P$			$2p\,^3P$			$3p\,^3P$	
[0045]	103.31	0.361	21.69	0.076		16.37	0.057		2.79	0.010
[0056]	46.41	0.365	9.65	0.076		6.68	0.053		1.12	0.009
[0067]	23.68	0.369	4.96	0.077		3.11	0.049		0.49	0.008
$l>6$	55.02		11.52			7.23			1.12	
[0144]	15.51	0.054	16.26	0.057		15.93	0.056		18.60	0.065
[0155]	6.75	0.053	7.01	0.055		6.53	0.051		8.09	0.064
[0166]	3.28	0.051	3.50	0.055		3.31	0.052		3.94	0.061
$l>6$	7.62		8.13			7.69			9.08	
Total	62.64		19.65			14.92			10.20	
	$3s\,^1S$		$3s\,^3S$			$3d\,^1D$			$3d\,^3D$	
[0044]	24.94	0.087	20.47	0.072	[0035]	14.16	0.049	[0442]	16.44	0.057
[0055]	10.74	0.084	8.70	0.068	[0046]	5.70	0.045	[0552]	7.31	0.057
[0066]	5.19	0.081	4.28	0.067	[0057]	2.98	0.046	[0662]	3.50	0.055
$l>6$	12.06		9.94			6.86			8.13	
					[0442]	14.05	0.049	[4413]	1.48	0.005
					[0552]	5.97	0.047	[5513]	0.68	0.005
					[0662]	2.76	0.043	[6613]	0.33	0.005
					$l>6$	6.41			0.76	
					[0044]	9.12	0.032			
					[0055]	3.11	0.025			
					[0066]	1.46	0.023			
					$l>6$	3.41				
					[0145]	3.74	0.013			
					[0156]	1.53	0.012			
					[0167]	0.70	0.011			
					$l>6$	1.63				
Total	12.06		9.94			18.31			8.89	

[a] It is the energy contributions from $[00ll]$, $[00l, l+1]$, $[01l, l+1]$, or $[00l-1, l+1]$ divided by that of $[ll]$ from the 318 term $1s1s$ core. See Ref. [39].

of higher-l contributions is carried out in the same way as in Ref. [27]. The details of extrapolation for each state are given in Table IV. The final results are included in Table I. The data in Table IV show that the $[00l, l+1]$ series in $2p\,^1P$ has the largest energy contribution. Fortunately, the convergence pattern of this series is very similar to that of the core, i.e., the ratio of $[00l, l+1]/[ll]$ is close to a constant. Hence the accuracy of the higher-l contribution can be estimated to a few percent. Other series, such as those of $2p\,^3P$ or the $[00ll]$ of $3s\,^{1,3}S$, the ratios are less stable. The uncertainty of the extrapolated results could be as much as 10%.

When we summed up the energies from the basic wave function, the core correction, the restricted variational, and higher-l extrapolation, the total nonrelativistic energies are obtained. These energies are given in Table I. They are substantially lower than the results from the literature [22, 21, 26]. Even the upper bound E_b's in Table I are lower than the corresponding energies in the literature by about 0.0485 ± 0.0011 a.u. We find that all the discrepancies fall within such a small range rather interesting. A large part of these discrepancies is probably coming from the $1s^2$ core which may not be adquately represented in the earlier theoretical works.

IV. RESULTS AND DISCUSSION

We use the same basis functions in Ψ_b to calculate the the energy contribution ΔE_{MP} from the mass polarization perturbation operator H_4. The isotope used in this work is ^{9}Be with $M = 9.012\,182\,2$ u (atomic mass unit) from Wapstra and Audi [40]. Recently the isotope shift of the ^{10}Be–^{9}Be $1s^22s^2$–$1s^22s3d\,^1D$ has been measured by Wen *et al.* [26] using high-resolution multiphoton-resonance-ionization mass spectroscopy. This shift can also be calculated using

$$\Delta\nu(^{10}\nu - {}^{9}\nu) = 2\,{}^{9}\mathcal{R}\,[\,^{10}\Delta E_{\mathrm{MP}}(1s^22s3d\,^1D) - {}^{10}\Delta E_{\mathrm{MP}}(1s^22s^2) - {}^{9}\Delta E_{\mathrm{MP}}(1s^22s3d\,^1D) + {}^{9}\Delta E_{\mathrm{MP}}(1s^22s^2)] + 2\,(^{10}\mathcal{R} - {}^{9}\mathcal{R})\,(E_{1s^22s3d^1D} - E_{1s^22s^2}) \qquad (15)$$

where $\mathcal{R}$ is the Rydberg constant and $\Delta\nu$ is in cm^{-1}. The first term on the right-hand side gives the specific mass shift whereas the second term is the normal mass shift [41].

In Table V the isotope shifts of ^{10}Be–^{9}Be and ^{8}Be–^{9}Be for all eight excited states are given. The shifts in this table are for transition energies to the ground state. The shift for transition between any two states can be derived from these data. The nuclear mass used is 10.0135341 u for ^{10}Be, and 8.0053051 u for ^{8}Be [40]. The electron mass is taken to be $5.485\,799 \times 10^{-4}$ u [42]. In Wen *et al.* [26], the ^{10}Be–^{9}Be $1s^22s^2$–$1s^22s3d\,^1D$ shift is measured to be 14.05(4) GHz. This agrees with our prediction of 14.076 GHz. Wen *et al.* used a slightly different nuclear mass data from ours. This causes a very small difference in the normal mass shift (at the fifth digit). For this reason, we compare with their measured isotope shift directly.

The relativistic corrections H_1, H_2, H_3, and H_5 are calculated with first-order perturbation theory. These scalar operators give corrections to the center of gravity energy. A very interesting question is whether the relativistic effects of the nl electron in the Be $1s^22snl$ system contribute to the "binding" or "antibinding" of this electron. We obtain this information by subtracting the relativistic correction of the $1s^22s$ state [39] from that of the $1s^22snl$. The result is shown in Table VI. It seems that the relativistic correction of the ns electron contributes to binding for both the singlet and triplet, but that of the np and nd electrons contributes to antibinding. This indicates that the relativistic effects of the nl ($l > 0$) are small by themselves, but their presence contributes to the shielding of the $2s$ electron and thus reduces the overall correction. The $2p$ electrons are most effective in shielding the $2s$ electron. This can also be seen from the results of Davidson *et al.* [43]. It is interesting to note that the antibinding in $1s^22s3d\,^1D$ is large. This is an indication of the presence of the $2p2p$ configuration in this state. By contrast, the antibinding effect in $1s^22s3d\,^3D$ is very small showing that the $2s$ electron is only shielded weakly by the $3d$ electron.

The QED effect from the nl electron is very small for beryllium. The QED contribution to the center of gravity energy for the $3s$ is about 0.03 cm^{-1}. It is much smaller for $l > 0$ electrons. The QED contribution of the $2p$ electron to the center of gravity energy of the $2s2p^{1,3}$ states is less than 0.01 cm^{-1}. Those of the $3p$ and $3d$ are even smaller.

If we sum the nonrelativistc energy $\mathrm{E}_{\mathrm{nonrel}}$, the $\Delta\mathrm{E}_{\mathrm{MP}}$, and the relativistic corrections, we obtain the relativis-

TABLE V. ^{10}Be–^{9}Be and ^{8}Be–^{9}Be isotope shifts for the $41s^22snl$–$1s^22s^2$ transitions [in GHz, $M(^{10}\mathrm{Be})$=10.013 534 1 u, $M(^9\mathrm{Be})$=9.012 182 2, u and $M(^8\mathrm{Be})$=8.005 305 1 u].

	$2p\,^1P$	$3s\,^1S$	$3p\,^1P$	$3d\,^1D$	$2p\,^3P$	$3s\,^3S$	$3p\,^3P$	$3d\,^3D$
$^{10}\nu$–$^9\nu$	8.776	10.362	13.388	14.076	12.003	9.405	11.925	11.524
Expt. [26]				14.05(4)				
MCHF [26]				14.158				
$^8\nu$–$^9\nu$	−11.039	−13.033	−16.839	−17.705	−15.097	−11.830	−14.998	−14.495

TABLE VI. Relativistic perturbation contributions to the binding of the nl electron in Be I $1s^22snl$ systems (in cm^{-1}). ΔE_{rel} is the sum of the expectation values of the relativistic perturbation operators. Negative energy implies binding. $\Delta E_{\text{rel}}(1s^22s) = -21.84\ \text{cm}^{-1}$ from Ref. [39]; $1s^22s^2$ result from Ref. [27].

nl state	$2s\,^1S$	$2p\,^1P$	$2p\,^3P$	$3s\,^1S$	$3s\,^3S$	$3p\,^1P$	$3p\,^3P$	$3d\,^1D$	$3d\,^3D$
$-\Delta E_{\text{rel}}(1s^22snl)$	29.62	16.83	16.24	22.72	23.09	18.59	20.74	17.59	21.52
$\Delta E_{\text{rel}}(1s^22snl) - \Delta E_{\text{rel}}(1s^22s)$	−7.78	5.01	5.60	−0.88	−1.25	3.25	1.10	4.25	0.32

tic energy of the $1s^22snl$ state. Subtracting this energy from that of the $1s1s$ core and adding the QED effect, we obtain the two-electron ($2snl$) IP. The corresponding energies for the $1s1s$ core are the same as those of Ref. [27]. They are not repeated in this table (Table VII). The IP of the nl electron is obtained by subtracting the predicted $2s$ IP, 146 883.08 cm^{-1} [27] from the $2snl$ IP. The excitaion energy of the $1s^22snl$ state is obtained by subtracting this nl IP from 75 192.07 cm^{-1}, the experimental IP of the $1s^22s^2$ [25]. These results are presented in Table VII.

Judging from the comparison of the predicted excitation energy with that of Johansson [25], it seems that the results for the S states and the triplets are quite good. The $2s2s\,^1S$–$2s2p\,^3P_1^o$ transition has been observed by Bozman *et al.* [44] at 21 978.92±0.01 cm^{-1}. Using the fine-structure results of Johansson [25], the $2p\,^3P^o$ center of gravity energy is found to be 21 980.15 cm^{-1} [45]. Our prediction, 21 980.85 is too high by 0.70 cm^{-1}. The discrepancy for the $3s\,^{1,3}S$ states is also within 1 cm^{-1}. Considering the extrapolation methods we used in this work, the uncertainty in the predictions could be close to 1 cm^{-1}. At present, these agreements are probably as good as one can hope for. The discrepancy for the predicted excitation energies of $3p\,^3P^o$ and $3d\,^3D$ is about 1.5 cm^{-1}.

The largest disagreement between prediction and experiment is for $3d\,^1D$. The discrepancy, 7.38 cm^{-1}, is larger than expected. To find the correlation energy for this state is particularly challenging because the mixing of the $2p2p$ and $2s3d$ configurations. We believe the error comes from our nonrelativistic energy. Even though we have used the restricted variation method with an extensive Ψ_2 to saturate the functional space, our result indicates that some important basis functions may still be missing in our wave function. We should mention that to calculate each of these excited states to the accuracy required in this work is very laborious. For example, to saturate the functional space for $3d\,^1D$, 27 restricted variation calculations are carried out. Each calculation includes many angular-spin components of the same $[l_1l_2l_3l_4]$. Several hundred linear parameters are used for each saturation wave function. The optimization of the nonlinear parameters in these wave functions also takes up considerable amount of computer time. We still lack a method to ensure that our basis functions will cover the entire functional space as in the case of B-spline method [1,46]. The discrepancies for the $2s2p\,^1P^o$ and $2s3p\,^1P^o$ excitation energies are 3.45 and 6.72 cm^{-1}. These results show clearly that we have not overcome the challenge of finding all of the correlation energy for these four-electron systems. Much effort is still needed to accomplish this goal.

Even though the relativistic corrections for beryllium excited states are considered to be small, a closer examination reveals how important these corrections are in precision predictions. For example, in Table VII, the excitation energy of the $3d\,^1D$ is "higher" than that of the experiment by 7.38 cm^{-1}. However, if we only compare its nonrelativistic energy, $-14.373\,790$ a.u. with that of the ground state, $-14.667\,349$ a.u. [27], the excitation energy would be 64 424.9 cm^{-1}. This is 3.4 cm^{-1} *lower* than the experiment. The same nonrelativistic energy comparison for $2p\,^1P^o$ and $3p\,^1P^o$ gives excitation energies which are also 8.7 and 3.1 cm^{-1} *lower* than the experiment. This shows that even for low-Z system such as beryllium, a meaningful comparison with experiment can only be made after the relativistic correction is considered.

In this work, the fine-structure splittings of the triplet states are calculated with the H_{so}, H_{soo}, and H_{ss} operators using first-order perturbation theory. The experimental Be $2s2p\,^3P_J^o$ splittings are 2.35 ($J = 2 \rightarrow 1$) and 0.64 ($J = 1 \rightarrow 0$) cm^{-1} [25]. They agree well with our predictions, 2.360 and 0.637 cm^{-1}. These results are given in Table VIII. Although many theoretical studies have been done on the Be I excited systems, not many theoretical fine-structure results are published. One exception is Laughlin, Constantinides, and Victor [23]. They use a model potential calculation and predict the splittings to be 2.53 and 0.71 cm^{-1}. These results should be considered as quite good in view of the simplicity in their computation. Correlation is quite important for calculating these fine structures. We have tried to compute the splittings for this $^3P^o$ using only the Ψ_0, the results are 2.00 and 0.48 cm^{-1}.

In the experiment of Johansson [25], the splitting of $1s^22s3p\,^3P_J^o$ ($J = 1, 0$) is not resolved. But the splitting from the $J = 2$ state to the $J = 1, 0$ is determined to be 0.37 cm^{-1}. In this work, we find that the splittings are 0.351 ($J = 2 \rightarrow 1$) and 0.091 ($J = 1 \rightarrow 0$) cm^{-1}. This implies that the predicted splitting from $J = 2$ to the center of gravity of $J = 1$ and 0 should be 0.374 cm^{-1}. It agrees with the experiment. The $2s3d\,^3D_J$ states are not resolved experimentally. The reason is very clear from Table VIII. The predicted splittings are 0.027 ($J = 3 \rightarrow 2$) and -0.023 ($J = 2 \rightarrow 1$). All three levels lie within a range of 0.027 cm^{-1}.

The oscillator strengths f of the beryllium excited systems have been studied extensively in the literature. We have also calculated some of the f values for the eight excited systems. The dipole length results and the corresponding transition rates are given in Table IX. Since this is not the main interest of the present work, we will not make an effort to compare the extensive data in the literature except to say that with the exception of $2s2s$–$2s3p\,^1P^o$ transition they agree well with the accurate results in the literature. We refer the interested reader to the recent work of Chang [1] on these comparisons.

The $2s2s$–$2s3p\,^1P^o$ f value obtained in this work is very small. The dipole length result is 0.009 14 and the dipole velocity result is 0.009 07. It is smaller than the f value of Stewart [10] and Victor and Laughlin [9] by more than a factor of 2, but it is larger than that of Altick and Glassgold [47] by a factor of 3. The small f value indicates large cancellation in the integral of transition matrix element. A reliable result can only be obtained if the two wave functions are accurate in spaces where overlap is significant.

The $2s2s$–$2s2p\,^3P_1^o$ transition has been observed by Bozman *et al.* [44]. It would be interesting to find out the lifetime of this state. The $2s2p\,^1P_1^o$ and $2s2p\,^3P_1^o$ can couple via $H_{\rm so}$ and $H_{\rm soo}$ operators. The coupling constant is given by

$$C_{\rm so+soo} = \frac{\langle\Psi(^1P_1^o)|H_{\rm so}+H_{\rm soo}|\Psi(^3P_1^o)\rangle}{E(^1P_1^o)-E(^3P_1^o)}. \tag{16}$$

TABLE VII. Ionization potential and excitation energy of the $1s^22snl$ states of beryllium. Columns three–four and six–seven are the energy difference between the $1s^22snl$ state and the $1s^2$ core. For other notations, see discussion in text.

	E (μa.u.)	IP (μa.u.)	IP (cm^{-1})	E (μa.u.)	IP (μa.u.)	IP (cm^{-1})
		$2p\,^1P$			$3p\,^1P$	
$E_{\rm nonrel}$	−14 473 434.91	817 868.70	179 490.50	−14 393 113.33	737 547.12	161 863.03
$\Delta E_{\rm MP}$	26.57	−0.86	−0.19	24.45	1.26	0.28
$\langle H_1+H_2\rangle$	−2 517.94	88.33	19.39	−2 524.50	94.89	20.83
$\langle H_3\rangle$	273.36	−8.12	−1.78	274.25	−9.01	−1.98
$\langle H_5\rangle$	−43.52	−3.51	−0.77	−45.83	−1.21	−0.26
Subtotal	−14 475 710.99[a]	817 944.54	179 507.14	−14 395 399.52[a]	737 633.06	161 881.88
QED Corr.		−3.6	−0.79		−3.6	−0.79
$2snl$ IP		817 940.9	179 506.35		737 629.5	161 881.09
nl IP[b]		148 651.6	32 623.27		68 340.1	14 998.01
E (excitation)[c]		193 969.5	42 568.80		274 281.0	60 194.06
Johansson [25]			42 565.35			60 187.34
Theor.–Expt.			3.45			6.72
		$2p\,^3P$			$3p\,^3P$	
$E_{\rm nonrel}$	−14 567 238.30	911 672.09	200 076.71	−14 398 960.12	743 393.91	163 146.17
$\Delta E_{\rm MP}$	15.96	9.75	2.14	26.32	−0.61	−0.13
$\langle H_1+H_2\rangle$	−2 519.40	89.79	19.70	−2 533.69	104.08	22.84
$\langle H_3\rangle$	273.12	−7.88	−1.73	275.03	−9.79	−2.15
$\langle H_5\rangle$	−39.14	−7.90	−1.73	−47.28	0.25	0.05
Subtotal	−14 569 522.31[a]	911 755.85	200 095.09	−14 401 254.30[a]	743 487.84	163 166.78
QED Corr.		−3.6	−0.79		−3.6	−0.79
$2snl$ IP		911 752.2	200 094.30		743 484.2	163 165.99
nl IP [b]		242 462.9	53 211.22		74 194.9	16 282.91
E (excitation)[c]		100 158.2	21 980.85		268 426.2	58 909.16
Bashkin and Stoner [45]			21 980.15			58 907.62
Theor.–Expt.			0.70			1.54
		$3s\,^1S$			$3d\,^1D$	
$\mathrm{E}_{\rm nonrel}$	−14 418 237.12	762 670.91	167 376.72	−14 373 790.47	718 224.27	157 622.41
$\Delta E_{\rm MP}$	27.52	−1.81	−0.40	24.58	1.13	0.25
$\langle H_1+H_2\rangle$	−2542.62	113.01	24.80	−2 519.71	90.10	19.77
$\langle H_3\rangle$	275.84	−10.60	−2.33	273.73	−8.48	−1.86
$\langle H_5\rangle$	−48.19	1.15	0.25	−45.59	−1.44	−0.32
Subtotal	−14 420 539.12[a]	762 772.66	167 399.05	−14 376 072.01[a]	718 305.56	157 640.25
QED Corr.		−3.7	−0.82		−3.6	−0.79
$2snl$ IP		762 768.9	167 398.24		718 302.0	157 639.46
nl IP[b]		93 479.6	20 515.16		49 012.6	10 756.38
E (excitation)[c]		249 141.5	54 676.91		293 608.5	64 435.69
Johansson [25]			54 677.26			64 428.31
Theor.–Expt.			−0.35			7.38
		$3s\,^3S$			$3d\,^3D$	
$E_{\rm nonrel}$	−14 430 064.40	774 498.19	169 972.35	−14 384 622.60	729 056.39	159 999.64
$\Delta E_{\rm MP}$	28.26	−2.55	−0.56	27.80	−2.09	−0.46
$\langle H_1+H_2\rangle$	−2 544.14	114.53	25.14	−2 536.14	106.53	23.38
$\langle H_3\rangle$	276.07	−10.83	−2.38	275.19	−9.95	−2.18
$\langle H_5\rangle$	−48.54	1.51	0.33	−48.49	1.46	0.32
Subtotal	−14 432 367.31[a]	774 600.85	169 994.88	−14 386 918.80[a]	729 152.34	160 020.70
QED Corr.		−3.8	−0.82		−3.6	−0.79
$2snl$ IP		774 597.1	169 994.06		729 148.7	160 019.90
nl IP[b]		105 307.8	23 110.98		059 859.4	13 136.82
E (excitation)[c]		237 313.4	52 081.09		282 761.7	62 055.25
Johansson [25]			52 080.94			62 053.72
Theor.–Expt.			0.15			1.53

[a] Our $1s^2$ relativistic contribution deviates from that of Pekeris [53] by −14.55 μa.u. This correction is added to the total energy.

[b] Obtained by subtracting the $1s^22s$ IP of 669 289.3 μa.u. or 146 883.08 cm^{-1} [27].

[c] Obtained by subtracting the nl IP from the $1s^22s^2$ IP of 342 621.1 μa.u. or 75 192.07 cm $^{-1}$ [52].

TABLE VIII. Fine-structure splitting for the triplet states of beryllium (in cm^{-1}).

$2p\,^3P_J$				Splitting		
J value	2	1	0	2-1	1-0	
E_J [a]	21981.967	21979.609	21978.973	2.358	0.636	
ΔE_J (QED)	0.001	−0.001	−0.002	0.002	0.001	
Total	21981.968	21979.608	21978.971	2.360	0.637	
Expt.[b]				2.35	0.64	
Other theory[c]				2.53	0.71	
$3p\,^3P_J$						
J value:	2	1	0	2-1	1-0	2-1,0
E_J [a]	58909.302	58908.952	58908.860	0.351	0.091	0.374
Expt.[b]						0.37
$3d\,^3D_J$						
J value	3	2	1	3-2	2-1	
E_J [a]	62055.256	62055.229	62055.252	0.027	−0.023	

[a] The excitation energy calculated with H_{so}, H_{soo}, and H_{ss} using first-order perturbation theory.

[b] Johansson [25].

[c] Laughlin, Constantinides, and Victor [23].

$C_{\mathrm{so+soo}}$ is found to be 0.8043×10^{-4} in this work. The f value of the $2s2s\,^1S$–$2s2p\,^3P_1^o$ transition can be expressed in terms of the f value of $2s2s\,^1S$–$2s2p\,^1P^o$ by

$$f_{(2p^3P_1^o-^1S)} = |C_{\mathrm{so+soo}}|^2 f_{(2p^1P^o-^1S)} \frac{\Delta E_{(2p^3P_1^o-^1S)}}{\Delta E_{(2p^1P^o-^1S)}}. \tag{17}$$

This gives an absorption $f_{(2p^3P_1^o-^1S)}$-value of 4.590×10^{-9}. The emission rate is found to be $0.4928\ \mathrm{sec}^{-1}$. This is larger than the $0.269\ \mathrm{sec}^{-1}$ of Laughlin, Constantinides, and Victor [23], the $0.174\ \mathrm{sec}^{-1}$ of Mühlethaler and Nussbaumer [48], but smaller than the $0.71\ \mathrm{sec}^{-1}$ of Garstang and Shamey [49].

V. CONCLUSION

In this work, we have made an *ab initio* computation for the energies of the excited $2snl$ ($n \leq 3$) four-electron systems. The purpose is to see whether the FCPC method is capable of predicting precise nonrelativistic energy for these systems. This question is relevant in view of the recent success of FCPC on the ground state of four-electron systems [27]. We choose the low-lying excited states of beryllium partly because accurate experimental data are available and the $2p\,^3P_1^o$–$2s\,^1S$ transition has been observed and partly because here the relativistic effects are small and the QED and higher-order relativistic effects are negligible. The correlation effects are particularly strong in these systems.

In addition to the FCPC, we have implemented a restricted variational method to calculate the nonrelativistic energy. For three- or more electron systems it is not always possible to use basis functions which are completely orthogonal. The advantage of this method over the conventional variational method is that it avoids the numerical instability caused by the linear dependence between the basis functions in Ψ_1 and Ψ_2. For a theoretician who uses variational method, this numerical instability could be most frustrating. In a precision calculation, the matrix size is quite large. Typically, they are well over 1000×1000. It takes a considerable amount of computer time to construct a secular equation. By the time this numerical instability becomes apparent, much valuable time is wasted.

Another advantage of the restricted variation method is that the calculation can be performed with *comparably* less computer resources. Since Ψ_b is reduced to one term, the matrix size is drastically reduced. The computation can be performed much faster. It is also a good method to find basis functions with large energy contributions, but they are inadvertently left out in Ψ_b. One can then include these basis functions in a new Ψ_b. In the absence of numerical instability, this makes it a potentially powerful method for accurate energy.

Judging from the Theor.- Expt. data in Table VII, the results for the S-excited states and for the triplet states are satisfactory. However, the agreement with experiment for $2p\,^1P^o$, $3p\,^1P^o$, and $3p\,^1D$ still needs to be

TABLE IX. The transition rates and lifetimes of the $1s^2 2snl$ states of beryllium.

Nonrelativistic transition	f	Transition rate (in $10^7\ \mathrm{sec}^{-1}$)	Lifetime (in nsec)
$2p\,^1P$-$2s\,^1S$	1.374	55.34	1.807
$3s\,^1S$-$2p\,^1P$	0.1175	3.452	28.97
$3p\,^1P$-$2s\,^1S$	0.00914	0.7361	72.30[a]
$3p\,^1P$-$3s\,^1S$	0.9565	0.6466	
$3d\,^1D$-$2p\,^1P$	0.4018	7.691	12.22
$3d\,^1D$-$3p\,^1P$	0.681	0.490	
$3s\,^3S$-$2p\,^3P$	0.0806	14.62	6.840
$3p\,^3P$-$3s\,^3S$	0.1127	1.167	85.69
$3d\,^3D$-$2p\,^3P$	0.287	18.46	5.359
$3d\,^3D$-$3p\,^3P$	0.500	.198	
Spin-induced transition	f	**Transition rate (in sec^{-1})**	**Lifetime (in sec)**
$2p\,^3P_1$–$2s\,^1S$	4.590×10^{-9}	0.4929	2.029
Other theory			
Ref. [23]		0.269	
Ref. [48]		0.174	
Ref. [49]		0.71	

[a] Since the lower state $1s^2 2p2p\,^1D$ has not been considered, the lifetime should be slightly shorter than this value.

improved. The fact that our excitation energy is higher than the experiment indicates that we have not found all the correlation energy.

The expectation values calculated from the wave functions seem to be acceptable. The predicted isotope shift and fine structures all agree with accurate experiment. The oscillator strengths agree with the accurate data in the literature. There are still discrepancies on the lifetime of the $1s^22s2p\,^3P_1^o$ and on the f value of the $2s\,^1S$–$3p\,^1P^o$ transition. These discrepancies can only be resolved by future experiments.

Our results show that the problem of four-electron-system correlation energy has not been overcome in some cases. We should mention that to calculate the correlation energy for each of the states considered here is quite laborious and it consumes a considerable amount of computer time. Much patience is needed to carry out the restricted variational method. Our result suggests that a more effective procedure is needed to ensure that all the correlation energy of these four-electron states can be uncovered. This is crucial in order to make *ab initio* calculations on five- or more electron systems.

The results on the Be I $1s^22s2p\,^3P^o$ and $2s3p\,^3P^o$ states are encouraging. The energies of these low-lying $^3P^o$ states in the isoelectronic sequence are particularly important. Their transitions to the ground state have been observed for some systems, hence they form the essential link between the singlets and triplets. Their energies are needed to establish the correct Grotrian diagram [45]. There have been much interest on these $^3P^o$ states [44, 50, 51, 54]. The fact that we have predicted accurate energies and fine structures for beryllium is an encouraging sign that we should extend the calculation to other Z systems.

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation Grant No. PHY 90-20543 and INT 91-01761.

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