

Electron affinities of $1s^2 2s 2p^3 P^o$ and $1s^2 2p^2^3 P$ of beryllium

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(Received 17 April 1995)

The energies of $1s^2 2s 2p^2^4 P$ and $1s^2 2p^3^4 S^o$ of the beryllium anion are calculated by the methods of full core plus correlation (FCPC) and restricted variation. The relativistic corrections are calculated with first-order perturbation theory. This is an application of FCPC to a five-electron atomic system. The energies obtained are much lower than previously expected. Combined with the most accurate theoretical and experimental data, the electron affinities of beryllium $1s^2 2s 2p^3 P^o$ and $1s^2 2p^2^3 P$ are predicted to be 289.1(10) and 295.0(7) meV, respectively. The former is considerably larger than the recent measurement of 261(10) meV. The transition wavelength of $1s^2 2s 2p^2^4 P - 1s^2 2p^3^4 S^o$ is predicted to be at 2653.70(68) Å, compared to the experimental observation at 2653.01(9) Å. The oscillator strength and the radiative lifetime are also calculated.

PACS number(s): 31.15.Ar, 32.10.Hq, 32.70.Cs, 31.30.Jv

It has been demonstrated theoretically [1–7] that the negative beryllium ion has three metastable bound terms $1s^2 2s 2p^2^4 P$, $1s^2 2p^3^4 S^o$, and $1s 2s 2p^3^6 S^o$, which lie below their parent terms $1s^2 2s 2p^3 P^o$, $1s^2 2p^2^3 P$, and $1s 2s 2p^2^5 P$ of the neutral atom, respectively. Although the existence of the $^4 P$ and the $^4 S^o$ terms has been confirmed experimentally [8–12], discrepancies between the predicted and the observed physical quantities still remain.

With much effort in resolving the blending by the relatively intense line of Be $1s^2 2s 2p^3 P^o - 1s^2 2p^2^3 P$ at 2650.62 Å, Gaardsted and Andersen [10] identified the line at 2653.01(9) Å to be the transition $1s^2 2s 2p^2^4 P - 1s^2 2p^3^4 S^o$, which is the only bound-bound transition in Be⁻. Their identification implies that the electron affinity (EA) of $1s^2 2p^2^3 P$ is 4.2 meV larger than that of $1s^2 2s 2p^3 P^o$, in contradiction with Bunge [5], who predicted that the former is 10 meV smaller than the latter. Although Gaardsted and Andersen's transition energy was in agreement with the calculation by Beck and Nicolaides [4], the accuracy of the calculation was not sufficient for a definitive comparison with experiment. Theoretical values with an accuracy of a few meV were claimed. For $1s^2 2s 2p^3 P^o$, Bunge's EA, 276.1(65) meV [5], was considered as the most accurate calculation. But the contemporaneous experimental value, 195(90) meV, given by Kvale *et al.* [9] was not accurate enough to test Bunge's result. Recently, Tang *et al.* [11] determined the EA of $1s^2 2s 2p^3 P^o$ to be 261(10) meV, using photodetached-electron spectroscopy. Their result and Bunge's prediction [5] barely overlap due to the large uncertainty quoted.

If the EA of $1s^2 2p^2^3 P$ were accurately known, a closed loop check for the EA of $1s^2 2s 2p^3 P^o$ could be done by using the transition wavelengths of Gaardsted and Andersen [10]. Unfortunately, neither accurate experimental nor theoretical data for the EA of $1s^2 2p^2^3 P$ were available in the literature. Instead, the experimental data of the Be⁻ transition [10] and the EA of $1s^2 2s 2p^3 P^o$ [11] were used to establish the EA of $1s^2 2p^2^3 P$; and these data were adapted to test the approximation methods of recent calculations, e.g., by Froese Fischer [6] and Olsen, Pettersson, and Sundholm [7].

The present calculation intends to provide accurate results for the energies of $1s^2 2s 2p^2^4 P$ and $1s^2 2p^3^4 S^o$ to verify the experiments of Gaardsted and Andersen [10] and Tang *et al.* [11]. The methods of full core plus correlation (FCPC) [13] and restricted variation (RV) [14,15] are used. Previously, the combination of FCPC and RV has yielded accurate results for three- and four-electron systems. In this work, it is applied to the loosely bounded five-electron anion. The methodology was discussed in Refs. [13–16]; the details will not be repeated here. The Hamiltonian,

$$H_0 = \sum_{i=1}^5 \left[-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right] + \sum_{\substack{i,j=1 \\ i < j}}^5 \frac{1}{r_{ij}}, \quad (1)$$

is solved by the Rayleigh-Ritz variational method. The trial wave function is a linear combination of parametrized Slater-type orbitals in the *LS*-coupling scheme. For FCPC, it is given by

$$\psi_{\text{FCPC}} = \mathcal{A} \left[\psi_{1s1s}(1,2) \psi_{\omega}(3,4,5) + \sum_{\Omega} \phi_{\Omega}(1,2,3,4,5) \right], \quad (2)$$

where \mathcal{A} is the antisymmetrization operator, ψ_{1s1s} is a pre-calculated wave function of Be III $1s^2^1 S$, which is used as a single term for the core, and ψ_{ω} represents the outer-electron orbitals. The five-electron wave-function ϕ_{Ω} 's are constructed to account for intershell and intrashell correlations. The linear and nonlinear parameters in ψ_{ω} and ϕ_{Ω} are determined by variation procedure. For an accurate wave function, ψ_{FCPC} is expanded to include as many terms as possible. However, too many terms may lead to numerical instability in solving the secular equation. To overcome this problem, the RV method is used [14,15]. After a sufficiently accurate ψ_{FCPC} is obtained, it is frozen as a single term ψ_B in the succeeding RV calculation in which the trial wave function is given by

$$\psi_{\text{RV}} = C_B \psi_B(1,2,3,4,5) + \mathcal{A} \sum_S \phi_S(1,2,3,4,5), \quad (3)$$

TABLE I. Energies (in $\mu\text{a.u.}$) of $1s^22s2p^2^4P$ and $1s^22p^3^4S^o$ of the beryllium anion.

	$1s^22s2p^2^4P$	$1s^22p^3^4S^o$
Nonrelativistic energy		
$E_{\text{upperbound}}$	-14 577 530.3	-14 406 032.0
E_B	-14 577 233.2	-14 405 773.2
Δ_{RV}	-407(33)	-266(22)
Δ_l	-7(3)	-13(4)
Δ_{core}	-230.1	-230.1
E_{nonrel}	-14 577 877(36)	-14 406 282(26)
	-14 570 770 ^a	-14 400 170 ^a
	-14 573 085 ^b	-14 401 969 ^b
	-14 576 918(182) ^c	
Perturbative corrections		
Mass polarization	13.3	12.1
Mass variation and Darwin	-2 505.3	-2 442.2
Orbit-orbit	-37.2	-29.5
Electron contact	273.3	265.9
Δ_{mr}	-14.6	-14.6
E_{total}	-14 580 148(36)	-14 408 491(26)

^aBeck, Nicolaides, and Aspromallis, Ref. [2].^bBeck and Nicolaides, Ref. [4].^cBunge, Ref. [5].

where C_B is an expansion coefficient whose value is very close to 1. The RV method improves the *basic wave function* ψ_B by the *saturation wave function* ϕ_S , which takes the same form as ϕ_Ω but with different linear and nonlinear parameters. The variation procedure is restricted to the parameters in ϕ_S . If a particular component in ϕ_S is found to make a significant contribution to the energy, it is inserted into the basic wave function for a more accurate ψ_B . In the actual calculation, Eq. (3) is carried out one set at a time for the angular space spanned by various couplings of a given set of angular momenta $[l_1, l_2, l_3, l_4, l_5]$. In addition to the eigenvalue E_B of the final ψ_B , an extrapolated nonrelativistic energy is obtained by summing up E_B and the improvements from the RV calculations for every mutually orthogonal set $[l_1, l_2, l_3, l_4, l_5]$; note that this energy is no longer an upper bound to the nonrelativistic energy.

The mass-polarization correction is calculated to infinite order by inserting the operator into Eq. (1) and re-solving the secular equation; the eigenfunction is then used to calculate the relativistic contribution in the Breit-Pauli approximation by first-order perturbation theory. These operators are the five-electron analogs of those in Refs. [13,15]. The conversion factors used are $\mathcal{R}_m(^9\text{Be}) = 109\,730.634 \text{ cm}^{-1}$ and $1 \text{ cm}^{-1} = 0.123\,984\,24 \text{ meV}$.

The Be III $1s^2^1S$ wave function in Ref. [15] is used as the core in Eq. (2) for the present calculation. For $1s^22s2p^2^4P$, the angular-momentum sets considered for ψ_ω include $[0,1,1]$, $[1,1,2]$, and $[0,2,2]$; those for ϕ_Ω and ϕ_S are $[0,0,0,l,l]$, $[0,0,1,l,l+1]$, and $[0,1,1,l,l]$ with $l=1-6$, and other selected eight sets of $\sum_i l_i \leq 8$. For $1s^22p^3^4S^o$, they are $[1,1,1]$ and $[1,2,2]$; $[0,0,1,l,l]$ and $[1,1,1,l,l]$, with $l=1-6$; $[0,1,1,l,l+1]$, with $l=1-5$; $[0,0,2,l,l+1]$, with $l=2-4$; and three other sets of $\sum_i l_i \leq 9$. The number of terms in the final ψ_B is 1039 for $1s^22s2p^2^4P$ and 1044 for $1s^22p^3^4S^o$. The details of the contribution of each angular-momentum set will be supplied to the interested reader upon

request. In Table I, Δ_{RV} is the improvement from the RV calculation with an additional 66(33) and 44(22) $\mu\text{a.u.}$ estimated for the truncation error due to the finite basis set for $1s^22s2p^2^4P$ and $1s^22p^3^4S^o$, respectively, and Δ_{core} is the core compensation as explained in Ref. [13]. The quantity Δ_l is estimated empirically for the contributions from high angular momenta ($l > 6$). The nonrelativistic energy E_{nonrel} is the sum of E_B , Δ_{RV} , Δ_l , and Δ_{core} . Compared with other theoretical data, the present energies are much lower. For $1s^22s2p^2^4P$, the best previous results, $-14.574\,450 \text{ a.u.}$ for the upper bound and $-14.576\,918(128) \text{ a.u.}$ for the extrapolated energy given by Bunge [5], are both higher than the E_B , $-14.577\,233 \text{ a.u.}$, from the present calculation.

The mass-polarization and relativistic corrections are presented in Table I. Here Δ_{mr} represents a small correction due to the inaccuracy of the core wave function (see Table V, Ref. [17]). By summing up E_{nonrel} and these corrections, the total energy is $-14.580\,148(36) \text{ a.u.}$ for $1s^22s2p^2^4P$ and $-14.408\,491(26) \text{ a.u.}$ for $1s^22p^3^4S^o$.

The accurate EA's of $1s^22s2p^3P^o$ and $1s^22p^2^3P$ can be determined by comparing the total energies of the two terms with those of the anions in Table I. The energy of $1s^22s2p^3P^o$ is $-14.569\,522 \text{ a.u.}$ [15], and that of $1s^22p^2^3P$ is $-14.397\,648 \text{ a.u.}$ [18]. The former agrees with accurate experiments to within 1 cm^{-1} . Both of the values are calculated by the FCPC and the RV methods as in this work. The EA's are predicted to be 289.1(10) meV for $1s^22s2p^3P^o$ and 295.0(7) meV for $1s^22p^2^3P$. For $1s^22s2p^3P^o$, the present result is much larger than the value of 261(10) meV by Tang *et al.* [11] from the photodetachment experiment. A comparison of the EA from different approaches is given in Table II.

In Tang *et al.* [11], the energy of the autodetached electron of $1s^22s2p^2^4P$ via the $1s^22s^2 \text{ } \epsilon s, d$ channels was also measured. They obtained 2.463(21) eV. Using the photon

TABLE II. Electron affinities (in meV) of $1s^2 2s 2p^3 P^o$ and $1s^2 2p^2^3 P$ of beryllium.

$1s^2 2s 2p^3 P^o$	$1s^2 2p^2^3 P$	Reference
Experiment		
195(90)		Kvale <i>et al.</i> [9]
261(10)		Tang <i>et al.</i> [11]
Theory		
240(100)		Weiss [1]
285	262	Bunge <i>et al.</i> [3]
217(57)	220(41)	Beck and Nicolaides [4]
276.1(65)		Bunge [5]
285(5)	286(5)	Olsen, Pettersson, and Sundholm [7]
289.1(10)	295.0(7)	This work, for center of gravity
288.9(10)	294.7(7)	This work, for $J=0$ level

spectroscopic value of 2.725 eV for the excitation energy of $1s^2 2s 2p^3 P^o$, they again established the EA of $1s^2 2s 2p^3 P^o$ to be 262 meV, which is consistent with their photodetachment result. However, Table II shows a substantial discrepancy between theory and experiment. Because most of the theoretical works involve some kinds of approximation or extrapolation methods, it is important to reexamine the discrepancy with a theoretical value free from possible errors introduced by the approximation methods. In this regard, EA's using only the upper bound will be particularly meaningful.

To obtain a better upper bound than the E_B in Table I, the size of the ψ_{1s1s} core in ψ_B is expanded from 159 to 298 terms; and those ϕ_S 's of significant contributions from each $[l_1, l_2, l_3, l_4, l_5]$ set are collected to form one single ψ_{RV} [see Eq. (3)]. The number of terms included in ϕ_S 's is 2006 for $1s^2 2s 2p^2^4 P$ and 1726 for $1s^2 2p^3^4 S^o$. The eigenvalues obtained are labeled $E_{\text{upperbound}}$ in Table I. By combining the upper bound with the perturbative corrections in Table I, the energy is $-14.579\,786$ a.u. for $1s^2 2s 2p^2^4 P$ and $-14.408\,225$ a.u. for $1s^2 2p^3^4 S^o$.

Next, an "experimental" energy is established for $1s^2 2s 2p^3 P^o$. Since the present calculation does not include the contribution from the QED effect, we start from the Be III $1s^2$ relativistic energy of Pekeris [19]. By subtracting the experimental ionization potentials of $1s^2 2s$ and $1s^2 2s^2$ and adding the experimental excitation energy of $1s^2 2s 2p^3 P^o$ from the data tables [20,21], an "experimental" energy, $-14.569\,516$ a.u., of $1s^2 2s 2p^3 P^o$ is obtained. Based on this datum and the upper bound result for $1s^2 2s 2p^2^4 P$, the EA of $1s^2 2s 2p^3 P^o$ is 279.4 meV, which is much larger than the experimental value of 261(10) meV by Tang *et al.* [11]. Alternatively, from the upper bound result for $1s^2 2p^3^4 S^o$ and the transition energy of $1s^2 2s 2p^2^4 P - 1s^2 2p^3^4 S^o$, the energy of $1s^2 2s 2p^2^4 P$ is $-14.579\,927$ a.u. The corresponding EA of $1s^2 2s 2p^3 P^o$ is 283.3 meV, again larger than the value of Tang *et al.* [11].

The predicted transition energy of $1s^2 2s 2p^2^4 P - 1s^2 2p^3^4 S^o$ in this work is $37\,672.1(97)$ cm^{-1} or $\lambda_{\text{air}} = 2653.70(68)$ \AA , which is in agreement with the observation at $2653.01(9)$ \AA [10]. In Table III, the result is compared with other predictions. Most of the wavelength predictions are quite close. However, an accurate energy difference does not imply that the energy values and the wave functions are also

TABLE III. Transition energy λ and upper term lifetime τ of $1s^2 2s 2p^2^4 P - 1s^2 2p^3^4 S^o$ of the beryllium anion.

λ (\AA)	τ (ns)	Reference
Experiment		
2653.01(9)	1.25(10)	Gaardsted and Andersen [10]
Theory		
2671	1.49	Beck, Nicolaides, and Aspromallis [2]
2638		Bunge <i>et al.</i> [3]
2654		Beck and Nicolaides [4]
2653.2		Froese Fischer [6]
2650.4(28)		Olsen, Pettersson, and Sundholm [7]
2653.70(68)	1.53	This work

accurate. In this work, the absorption oscillator strength f and the radiative transition rate are also calculated. The dipole-length result is $f_L = 0.231$ and the dipole-velocity result is $f_V = 0.228$. The transition rate from the dipole-length formula is $6.54 \times 10^8 \text{ s}^{-1}$. In the absence of other decay mechanisms, it would mean a radiative lifetime of 1.53 ns, which is 22.4% longer than the measurement of 1.25(10) ns [10] (see Table III).

A very similar theory-experiment discrepancy appears in the anion transition $\text{Li}^- 1s 2s 2p^2^5 P - 1s 2p^3^5 S^o$. Recently, the energies and wave functions of $\text{Li}^- 1s 2s 2p^2^5 P$ and $1s 2p^3^5 S^o$ have been calculated to high accuracy by Yang and Chung [22]. The predicted radiative lifetime 2.910 ns agrees with the 2.86(10) ns from Bunge's calculation [23]. But it is longer than the experimental value 2.3(1) ns [24] by about 26%. This discrepancy completely disappears for the same transition in other four-electron atomic systems ($4 \leq Z < 8$). A very interesting similarity between $\text{Be}^- 1s^2 2p^3^4 S^o$ and $\text{Li}^- 1s 2p^3^5 S^o$ is that they have about the same electron binding energy. Using the accurate energy $-5.256\,654$ a.u. [22] for $\text{Li}^- 1s 2p^3^5 S^o$ and $-5.245\,967$ a.u. [16] for $\text{Li} 1s 2p^2^4 P$, the EA of $\text{Li} 1s 2p^2^4 P$ becomes 290.7 meV, which is very close to the 295.0 meV for $\text{Be} 1s^2 2p^2^3 P$. Assuming room temperature for the experiment, these EA's appear to be too large for the detachment induced by blackbody radiation to account for the lifetime discrepancy. A channel that is open only to the negative ions is the radiative autodetachment. Its contribution to the $\text{Li}^- 5S^o$ lifetime is 5%, according to Beck and Nicolaides [25]. This is too small to account for the discrepancy.

In Table IV, the result for the fine-structure correction to the center-of-gravity energy of $1s^2 2s 2p^2^4 P$ is presented. Usually, the experimental EA is given for the $J=3/2$ level. The shift from the center-of-gravity energy to $^4P_{3/2}$ is only 0.02 meV.

It is interesting to compare the size of the anion with the neutral atom. For $1s^2 2s 2p^2^4 P$, $\langle \sum_i r_i \rangle = 12.324 a_0$ and $\langle \sum_i r_i^2 \rangle = 63.862 a_0^2$, where a_0 is the Bohr radius. For $1s^2 2p^3^4 S^o$, the values are $13.654 a_0$ and $79.970 a_0^2$, respectively. By subtracting the corresponding values, $0.8286 a_0$ and $0.4641 a_0^2$, of the core, the average values of $\langle r \rangle$ and $\langle r^2 \rangle$ for each valence electron are $3.832 a_0$ and $21.133 a_0^2$ for $1s^2 2s 2p^2^4 P$, and $4.275 a_0$ and $26.502 a_0^2$ for $1s^2 2p^3^4 S^o$. By using the wave functions in Refs. [15,18], the corre-

TABLE IV. First-order perturbative contributions (in $\mu\text{a.u.}$) of spin-orbit (SO), spin-spin (SS), and spin-other-orbit (SOO) interactions to the center of gravity for each level J of $\text{Be}^- 1s^22s2p^2\ ^4P$.

J	SO	SS	SOO	Total
5/2	9.157	-0.1266	-7.096	1.935 1.823 ^a
3/2	-6.105	0.5064	4.731	-0.8677 -0.7723 ^a
1/2	-15.26	-0.6330	11.83	-4.068 -3.923 ^a

^aHartree-Fock calculation with correlated result, Beck and Nicolaides, Ref. [4].

sponding values of the neutral atoms are $2.699a_0$ and $8.873a_0^2$ for $1s^22s2p\ ^3P^o$, and $2.945a_0$ and $10.820a_0^2$ for $1s^22p^2\ ^3P$.

In summary, the FCPC method is applied to five-electron systems. The resulting energy uncertainty, about 1 meV, is slightly larger than those of the four-electron state calculations. Nevertheless, it represents at least an order of magnitude improvement over the best theoretical result in the literature.

On the electron affinity of $\text{Be } 1s^22s2p\ ^3P^o$, the present prediction clearly disagrees with the experiment of Tang *et al.* [11]. The disagreement persists even when theory uses

results from the upper bound calculation only.

Note added in proof. We have just learned that, in a very recent experiment by P. Kristensen, V. V. Petrunin, H. H. Andersen, and T. Andersen, the electron affinities of beryllium are determined to be 291.20(10) meV for $1s^22s2p\ ^3P^o$ and 295.70(25) meV for $1s^22p^2\ ^3P$; the transition wavelength is measured at 2653.18(8) Å. These results agree well with the corresponding values of this work. We are grateful to T. Andersen for informing us of these results prior to their publication.

This work is supported by National Science Foundation Grant No. PHY93-14907.

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