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Binding energy of the lowest state of negative beryllium

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Accurate eigenvalues of Schrödinger's nonrelativistic equation for Be $(1s^2 2s2p)^3P$ and Be$^-$ $(1s^2 2s 2p^2)^4P$ have been calculated yielding a corresponding electron affinity A of 276.1±6.5 meV. The absolute term value of Be$^-$ (relative to the Be ground state) obtained as the difference between the experimental term value of Be ^3P and A is 2.4492±0.0065 eV, in agreement with a recent measurement of 2.53±0.11 eV.

I. INTRODUCTION

Although the first beam of Be$^-$ was produced by Bethge, Heinicke, and Baumann more than ten years ago,[1] the first experimental characterization of negative beryllium came only in 1984, as Bae and Peterson[2] reported observing the metastable $(1s^2 2s 2p^2)^4P$ state of Be$^-$ and estimated its decay rate. Very recently, Kvale *et al.*[3] succeeded in measuring the energy level of this state by studying the energy spectra of electrons autoejected from a Be$^-$ ion beam.

Theoretical predictions of the existence of several states of Be$^-$, however, have been known for some time. By means of moderate-size configuration-interaction (CI) calculations, Weiss[4] predicted that Be$^-(1s^2 2s 2p^2)^4P$ is metastable and has a binding energy of 240±100 meV. Weiss's calculations also showed that Be$^-(1s^2 2s^2 3s)^2S$ is not stable, as confirmed later by Jordan and Simons[5] using second-order Rayleigh-Schrödinger perturbation-theory calculations. More recently, Bunge[6] predicted the existence of another state, the $(1s^2 2p^3)^4S^o$, which should decay to the $(1s^2 2s 2p^2)^4P$ by emitting uv radiation. On the basis of electron correlation calculations, Beck *et al.*[7] then characterized the bound states of Be$^-$ corresponding to the two configurations $(1s^2 2s 2p^2)^4P$ and $(1s^2 2p^3)^4S^o$ and predicted the existence of a core-excited sextet: $(1s2s2p^3)^6S^o$. A systematic search for excited states of negative ions by Bunge *et al.*[8] yielded quantitative electron affinities for the two valence-excited states of Be$^-$ on the basis of nonrelativistic fixed-core valence-shell CI calculations. In recent work by Beck *et al.*[9] the electron affinities of the two lowest bound states of the Be$^-$ ion were obtained by means of many-body calculations.

Because of the importance and novelty of negative ions of small systems, much experimental effort is being devoted to the obtaining and characterization of their bound states and possible transitions between them. Since theoretical calculations with uncertainties of a few meV are, although difficult, within the realm of present capabilities, we have performed such calculations for the $(1s^2 2s 2p^2)^4P$ state of Be$^-$ and for the $(1s^2 2s 2p)^3P^o$ state of Be (Fig. 1) in order to obtain a precise value for the electron affinity of the latter and to compare a calculated absolute term value for the lowest bound state of Be$^-$ with the one just measured at Oak Ridge National Laboratory.[3]

II. CALCULATION

The nonrelativistic energies E_{nr} were calculated variationally by means of CI wave functions,

$$\Psi = \sum_{K,p} \Phi_K^{(p)} a_{Kp} \,, \tag{1}$$

where the $\Phi_K^{(p)}$'s are successively orthogonalized projected Slater determinants $D_{K\alpha}$ made up of orthonormal spin orbitals,

$$\Phi_K^{(p)} = O(L^2,S^2) \sum_{\alpha=p}^{g_K} D_{K\alpha} b_{K\alpha}^{(p)} \,. \tag{2}$$

One- through four-electron excitations are considered. Degenerate configurations K, with degeneracies g_K, are

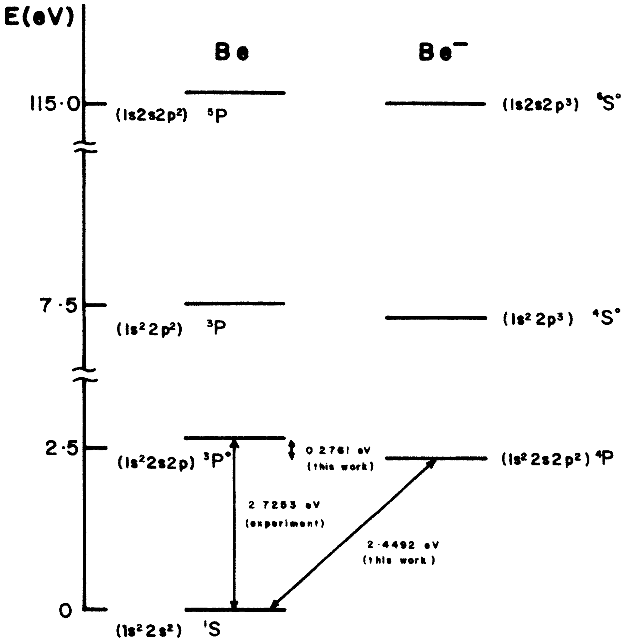

FIG. 1. Energy-level diagram for the Be$^-$ ion and relevant levels of BeI.

projected in a way that takes advantage of the minimum Hartree-Fock interacting space.[10,11]

We write the electron affinity A as

$$A = A_{\mathrm{nr}} + A_{\mathrm{RRMP}} , \tag{3}$$

where

$$A_{\mathrm{nr}} = E_{\mathrm{nr}}(\mathrm{Be}) - E_{\mathrm{nr}}(\mathrm{Be}^-) \tag{4}$$

is the difference between the nonrelativistic energies of the neutral and the negative species, and

$$A_{\mathrm{RRMP}} = E_{\mathrm{RRMP}}(\mathrm{Be}) - E_{\mathrm{RRMP}}(\mathrm{Be}^-) \tag{5}$$

includes relativistic, radiative, and mass-polarization corrections. A_{RRMP} contributions to electron affinities have been discussed before.[12] The bulk of the A_{RRMP} term is believed to be given by its relativistic part which does not exceed 1 meV until $Z=7$ in atomic nitrogen. We have then assigned $A_{\mathrm{RRMP}} \cong \pm 1$ meV $\cong \pm 0.000037$ a.u. for the Be$^-$ ion, yielding

$$A = A_{\mathrm{nr}} \pm 1 \text{ meV} . \tag{6}$$

The absolute term value T of Be$^-(1s^2 2s 2p^2)^4C$ with respect to the ground state of BeI is calculated as

$$T = \Delta E(2s^2 \rightarrow 2s2p\ ^3P) - A , \tag{7}$$

where $\Delta E(2s^2 \rightarrow 2s2p\ ^3P)$ is the experimental[13] term value of Be$(1s^2 2s2p)^3P$;

$$\Delta E(2s^2 \rightarrow 2s2p\ ^3P) = 2.7253 \text{ eV} . \tag{8}$$

T could also be obtained directly as

$$T = T_{\mathrm{nr}} + T_{\mathrm{RRMP}} \tag{9}$$

with

$$T_{\mathrm{nr}} = E_{\mathrm{nr}}[\mathrm{Be}^-(1s^2 2s 2p^2)] - E_{\mathrm{nr}}[\mathrm{Be}(1s^2 2s^2)] \tag{10}$$

if T_{RRMP} were known.

III. RESULTS

Accurate wave functions were obtained for Be$^-(1s^2 2s 2p^2)^4P$ and Be$(1s^2 2s 2p)^3P^o$. In both cases we started from analytical self-consistent wave functions of near Hartree-Fock accuracy. Energy-optimized Slater-type orbitals (STO's) were calculated separately for L-shell and intershell wave functions for the purpose of estimating converged pair energies. A shorter STO basis including all L-shell STO's and newly optimized intershell STO's was finally adopted to approximate the full CI expansion. Although several STO's obtained in this way are effective to account for K-shell correlations, no specific energy optimizations for K-shell STO's were carried out.

The error ΔE_{STO} due to truncations in the STO basis is calculated as a sum of three terms:

$$\Delta E_{\mathrm{STO}} = \Delta E_{\mathrm{STO}}(L) + \Delta E_{\mathrm{STO}}(I) + \Delta E_{\mathrm{STO}}(K) \tag{11}$$

corresponding to the L-shell, intershell, and K-shell expansions, respectively. STO truncation errors due to triple and higher-excited intershell excitations[14] are found to be insignificant at the present level of accuracy.

The final STO sets are given in Table I together with truncation energy errors. $\Delta E_{\mathrm{STO}}(L)$ is calculated as a sum of saturation remainders $\Delta E_l(L)$ computed at each step of the STO optimization for each l value (Table I). $\Delta E_{\mathrm{STO}}(I)$ is the sum of saturation remainders $\Delta\epsilon_l(I)$ for the optimized intershell STO basis plus a correction δ:

$$\Delta E_{\mathrm{STO}}(I) = \sum_l \Delta\epsilon_l(I) + \delta , \tag{12}$$

where δ is the energy difference between the L-shell and intershell wave functions calculated with the complete and the shorter STO basis, respectively.

Our largest truncation energy error, by far, is the K-shell correction $\Delta E_{\mathrm{STO}}(K)$. Since no STO's are optimized specifically for the K shell, it is not surprising that the K shell should not be very well represented in our final wave function. However, we can calculate with the final STO basis the Be$^{++}(1s^2)^1S$ energy $E(1s^2)$ and compare it with the exact value of Pekeris:[15]

$$E(\mathrm{Pekeris}) = -13.655566 \text{ a.u. } (^9\mathrm{Be}) . \tag{13}$$

$\Delta E_{\mathrm{STO}}(K)$ is then obtained as

$$\Delta E_{\mathrm{STO}}(K) = E(\mathrm{Pekeris}) - E(1s^2) . \tag{14}$$

This way of calculating $\Delta E_{\mathrm{STO}}(K)$ has been tested carefully in this work by verifying that additional STO's give the same energy contribution for a Be^{++} wave function as for either a Be or a Be$^-$ K-shell wave function.

Finally, natural orbitals (NO's) from a single and double CI wave function were obtained in order to approximate the full CI expansion in our final STO basis. In this basis of NO's, an exhaustive search was performed over single, double, triple, and unlinked quadruple excitations.

We find that only single excitations of the type

$$2s \rightarrow d ,$$

$$1s \rightarrow 2s ,$$

are important, both for Be and Be$^-$. The main configurations for Be$^-$ are double excitations of the type

$$(2p)^2 \rightarrow p^2, d^2 ,$$

$$2s2p \rightarrow sp, pd ,$$

$$(1s)^2 \rightarrow p^2, s^2, pp', ss' ,$$

$$1s2p \rightarrow pd .$$

Except for the $(2p)^2$ excitations, the same configurations are dominant in neutral Be. The f, g, and h angular correlation functions contribute 1277 microhartrees for Be$^-$ and 1066 microhartrees for BeI, mainly through excitations of the type

$$(2p)^2 \rightarrow f^2, g^2, h^2 ,$$

$$(1s)^2 \rightarrow f^2, g^2, h^2 ,$$

$$2s2p \rightarrow df, fg, gh ,$$

$$1s2p \rightarrow df, fg, gh ,$$

$$1s2s \rightarrow f^2, g^2, h^2 .$$

TABLE I. STO parameters for $Be^-(1s^22s2p^2)^4P$ and $Be(1s^22s2p)^3P^o$ and corresponding truncation errors in microhartrees, 1 microhartree $=10^{-6}$ a.u.

	l	STO parameters										$-\Delta E_l(L)$	$-\Delta\epsilon_l(I)$
$Be^-(^4P)$	0	$1s$:6.225	$1s$:3.437	$3s$:1.76	$2s$:0.88	$3s$:0.64	$4s$:1.225	$2s$:0.41	$3s$:4.00	$4s$:4.50		16±5	10±3
	1	$2p$:1.26	$2p$:0.88	$2p$:0.293	$3p$:1.68	$4p$:2.18	$5p$:0.50	$2p$:3.31	$3p$:3.73	$4p$:4.10	$5p$:6.10	20±8	8±4
	2	$3d$:1.10	$3d$:0.62	$4d$:1.19	$3d$:4.10	$3d$:1.72	$4d$:4.64	$5d$:5.00				8±3	12±4
	3	$4f$:1.00	$5f$:1.15	$4f$:3.60	$5f$:3.90							8±3	15±3
	4	$5g$:1.53	$5g$:4.90									16±3	9±2
	5	$6h$:1.90	$6h$:6.50									3±2	
	>5											2±2	2±2
							$-\Delta E_{STO}(L)=$ 73±26 $-\Delta E_{STO}(I)=$ 156±88 $-\Delta E_{STO}(K)=$1988±20						
$Be(^3P^o)$	0	$1s$:6.225	$1s$:3.437	$3s$:1.81	$2s$:0.87	$3s$:0.87	$4s$:1.35	$2s$:3.00	$3s$:3.40			4±1	6±2
	1	$2p$:1.21	$2p$:0.78	$3p$:0.38	$3p$:1.72	$4p$:2.18	$3p$:3.80	$4p$:3.80	$5p$:0.59	$4p$:6.30		4±1	6±2
	2	$3d$:1.01	$3d$:2.56	$4d$:1.18	$4d$:3.00	$5d$:6.20	$6d$:4.30					4±2	10±5
	3	$4f$:1.18	$4f$:3.80	$5f$:1.35	$5f$:4.05	$6f$:6.80						4±1	6±2
	4	$5g$:1.95	$5g$:4.90	$6g$:4.00								3±1	3±1
	5	$6h$:2.40	$6h$:5.50									2±1	4±2
	>5											1±1	4±2
							$-\Delta E_{STO}(L)=$ 22±8 $-\Delta E_{STO}(I)=$ 129±35 $-\Delta E_{STO}(K)=$2225±20						

TABLE II. Wave function and energy for the $(1s^22s2p^2)^4P$ state of Be$^-$ in a.u.: 1 a.u. (^{9}Be)=27.2099 eV.

Type of wave function	Energy
Self-consistent-field wave function $(5s,4p)$	−14.508 996
183 L-shell CI $(6s,6p,3d,2f,2g,1h)$	−14.529 335
227 intershell CI $(7s,6p,4d,3f,2g,1h)$	−14.513 903
501 K, L, and intershell CI with selected singles and doubles $(9s,10p,7d)$	−14.571 810
Contribution from f excitations	−0.001 121
g excitations	−0.000 123
h excitations	−0.000 034
triple excitations	−0.000 636
quadruple excitations	−0.000 977
669 K, L, and intershell CI with selected singles, doubles, triples, and quadruples $(9s,10p,7d,4f,2g,2h)$	−14.574 450
ΔE_{STO}	−0.002 217(132)
ΔE_{CI}	−0.000 251(50)
Estimated nonrelativistic energy E_{nr}	−14.576 918(182)

Other types of configurations involving f, g, and h orbitals were found to contribute, as a whole, less than 10 microhartrees for each one of these states.

The L-shell triple excitations of Be$^-$ contribute almost 400 microhartrees, which is more than 60% of the total triple contribution. The most important triple excitations are

$$2s(2p)^2 \rightarrow sp^2, spp', sd^2, sdd', p^2d, pp'd, d^3, d^2d'$$

and

$$(1s)^22s \rightarrow p^2d\ .$$

In BeI, only the $(1s)^22s$ excitations of the type

$$(1s)^22s \rightarrow p^2d, s^2d, ss'd$$

contribute significantly to the energy (about 260 microhartrees).

Only those quadruple excitations obtained as unlinked pairs[16] were considered. They account for almost 1000 microhartrees in Be$^-$ but only 69 microhartrees in BeI. This large difference is due, in part, to a better choice of natural orbitals in the second case, which gives a faster convergence. In the $1s^22s2p$ state of BeI, no doubly excited configuration has an appreciable coefficient in the CI expansion. In Be$^-$, on the other hand, the leading coefficient c_1 is 0.9819, and configuration $1s^22s(p')^2$ has a coefficient $c_2=-0.1193$. Thus, quadruple excitations involving the double excitation $(2p)^2 \rightarrow (p')^2$ contribute significantly. Wave functions and energies are presented in Tables II and III.

The error ΔE_{CI} due to the truncation of the CI expansion is calculated as a sum of variational energy differences between trial Ψ's and corresponding truncated wave functions, the latter being obtained by discarding expansion terms Φ_j on the basis of their partial energy contributions:[17]

$$\Delta E_j = c_j^2(E-H_{jj})/(1-c_j^2)\ . \tag{15}$$

Our best wave function for each state contains all terms with partial energy contributions larger or equal than 0.5 microhartree.

The nonrelativistic electron affinity A_{nr} of Be$(1s^22s2p)^3P^o$ is obtained as the difference between the corresponding E_{nr} values given in Tables II and III:

TABLE III. Wave function and energy for the $(1s^22s2p)^3P^o$ states of BeI in a.u.: 1 a.u. (^{9}Be)=27.2099 eV.

Type of wave function	Energy
Self-consistent-field wave function $(6s,5p)$	−14.511 488
49 L-shell CI $(6s,6p,2d,2f,1g)$	−14.518 659
256 intershell CI $(7s,6p,4d,3f,2g,1h)$	−14.516 392
498 K, L, and intershell CI with selected singles and doubles $(8s,9p,6d)$	−14.563 015
Contribution from f excitations	−0.000 896
g excitations	−0.000 091
h excitations	−0.000 019
triple excitations	−0.000 305
quadruple excitations	−0.000 069
452 K, L, and intershell CI with selected singles, doubles, triples, and quadruples $(8s,9p,6d,5f,3g,2h)$	−14.564 296
ΔE_{STO}	−0.002 376(63)
ΔE_{CI}	−0.000 099(30)
Estimated nonrelativistic energy E_{nr}	−14.566 771(93)

$$A_{\mathrm{nr}}=(-14.576\,918\pm0.000\,182)$$
$$-(-14.566\,771\pm0.000\,093)$$
$$=0.010\,147\pm0.000\,204 \text{ a.u.}=276.1\pm5.5 \text{ meV} .$$

Using Eq. (6), we get the following for the total electron affinity A:

$$A=276.1\pm6.5 \text{ meV} .$$

In Table IV this result is compared with those obtained in previous calculations and the recent experiment in Kvale *et al.*[3]

The absolute term value for $\mathrm{Be}^-(1s^2 2s 2p^2)^4P$ is calculated from Eq. (7) as

$$T=2.7253-(0.2761\pm0.0065)=2.4492\pm0.0065 \text{ eV} .$$

If Eq. (10) is used instead, we get

$$T_{\mathrm{nr}}=(-14.576\,918\pm0.000\,182)$$
$$-(-14.667\,328\pm0.000\,025)$$
$$=0.090\,410\pm0.000\,184 \text{ a.u.}$$
$$=2.4600\pm0.0050 \text{ eV} .$$

Since T_{RRMP} is not known precisely but is expected to be negative and of the order of a few meV, both results are in good agreement. A comparison between term values T obtained theoretically and experimentally is presented in Table V.

The correlation energy E_c of Be^- can also be estimated from our data. If we consider as a reference the numerical Hartree-Fock result reported by Beck *et al.*,[7] and use our estimate of the total nonrelativistic energy E_{nr}, we obtain

$$E_c=-14.509\,028-(-14.576\,918)=0.067\,890 \text{ a.u.}$$
$$=1.8473 \text{ eV} .$$

IV. CONCLUSIONS

In a recent calculation on He^-,[18] we obtained the electron affinity of $\mathrm{He}(1s2s)^3S$ with an accuracy of 0.04 meV. Obviously, this achievement cannot be repeated with a reasonable amount of effort for a five-electron system such as Be^-, and our electron affinity for $\mathrm{Be}(1s^2 2s 2p)^3P^o$ has an uncertainty 150 times larger than the one for $\mathrm{He}(1s2s)^3S$. Yet, this result is an order of magnitude more precise than the best available theoretical one and almost 20 times more precise than the experimental one.

TABLE IV. Comparison of values for the electron affinity (EA) of $\mathrm{Be}(1s^2 2s 2p)^3P^o$.

EA (meV)	Reference
240±100	Weiss, Ref. 4
>122	Beck *et al.*, Ref. 7
285	Bunge *et al.*, Ref. 8
217.7±57.1	Beck and Nicolaides, Ref. 9
190±110	Kvale *et al.*, Ref. 3
276.1±6.5	This work

TABLE V. Comparison of values for the absolute term energy of $\mathrm{Be}^-(1s^2 2s 2p^2)^4P$.

Term value (eV)	Reference
2.56±0.057	Beck *et al.*, Ref. 9
2.53±0.11	Kvale *et al.*, Ref. 3
2.4492±0.0065	This work

On the other hand, in a previous paper[8] we used a much simpler type of wave function to predict the existence of excited states of negative ions up to $Z=30$. Following the pioneering work of Weiss[4] and the systematic approach of Sasaki and Yoshimine,[19] the electron affinity was written as a sum of two terms,

$$A=A_{\mathrm{HF}}+A_c ,$$

and the correlation term A_c was, in turn, split into separate contributions, A_{c1}, corresponding to the outermost electron shell, A_{c2}, corresponding to the next shell, including intershell correlations with the outermost shell, and so on:

$$A_c=A_{c1}+A_{c2}+A_{c3}+\cdots .$$

It was found[8] that, for $A_c \cong A_{c1}$, the electron affinity of $\mathrm{Be}(1s^2 2s 2p)^3P^o$ is 285 meV, as compared with our more precise value of 276.1±6.5 meV. Introducing only part of A_{c2}, as Beck *et al.*,[9] gives a significantly lower result for A ($A=217.7$ meV). Since the K shells of both states involved are essentially the same, differences in the correlation effects which contribute to A_{c2} are mainly due to the intershell excitations and to the effects of the triple and quadruple excitations. The latter, in particular, are large ($\cong$977 microhartrees) in the case of Be^- and much smaller ($\cong$60 microhartrees) in the BeI parent state. So, it would seem that, unless A_{c2} is computed accurately, including triple and quadruple excitations, one might as well stop at the A_{c1} level.

Similar work is in progress for the states $(1s^2 2p^3)^4S^o$ of Be^- and $(1s^2 2p^2)^3P$ of BeI. An uncertainty of 6 meV in the transition energy between the two lowest states of Be^- will enable us to obtain the wavelength of the expected photons with a 3-Å accuracy. This number is still too large for experimental identification, and we plan to refine our calculations somewhat more in order to decrease the uncertainty in λ to about 1 Å, which means calculating the nonrelativistic energies to within less than 70 microhartrees.

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