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Recalibration of the Auger spectra of boron

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By using saddle-point technique, 12 autoionizing and two metastable autoionizing states of B III are calculated. To obtain high accuracy relativistic effects and mass polarization effect are included in the computation. Spin-orbit, spin—other-orbit, and spin-spin effects are also considered. Using the B IV $(1s^2)^1S$ result of Pekeris the corresponding Auger energies are tabulated. These data are then used to recalibrate the reported boron electron spectra of Rødbro, Bruch, and Bisgaard by about 0.15 eV. The calculated energies enable us to make seven new identifications in the boron Auger spectra. The fine-structure calculation also reveals many inverted J levels among these core-excited states.

I. INTRODUCTION

In an earlier work, Rødbro, Bruch, and Bisgaard[1] reported the high-resolution Auger spectra of Li, Be, B, and C which are excited in a single collision with gaseous target. With 100—500-keV Li^+, Be^+, B^+,and C^+ ions colliding on He and CH_4, the singly and doubly core-excited states are strongly populated. High resolution is obtained by selecting a small observation angle (6.4°) with respect to the beam axis. Numerous states, several of them previously not seen, have been reported. In particular, the doubly core-excited Li and Be^+ system has been accurately measured and reported for the first time. To understand the origin of these lines has been a most interesting and challenging problem for the various existing theories. These spectra are positively identified in recent work.[2,3]

In Rødbro *et al.* the lithium spectra are calibrated using the photoabsorption data of Ederer *et al.*[4] and the beryllium spectra are calibrated using the experimental result of Kennedy and Caroll.[5] However, no such accurate data are available for boron. Although there were theoretical calculations on the core-excited states of B III in the literature,[6–10], these are not accurate enough for calibration purposes. The lack of reliable theoretical data, the kinematic transformation from the laboratory to the source-particle frame, and the uncertainty in the space-charge potential makes an absolute calibration of the projectile Auger lines very difficult. Consequently, rather large uncertainties of the Auger peak energies were resulted. Since the experimental results of Rødbro *et al.* represent the only high-resolution boron Auger spectra reported in the literature, it is highly desirable to recalibrate these spectra accurately so that the error bars can be significantly reduced.

II. COMPUTATION AND RESULTS

Recently, a new theoretical method has been developed for calculating the autoionizing states of the atomic system. This saddle-point method[11] has been carried out extensively for Li, Be^+, and He^- in the elastic, inelastic, as well as triply excited, energy region. For narrow resonances, the calculated energy usually agrees with the accurate experimental data to well within 0.05 eV and in many cases to less than 0.01 eV.[12,13] Hence, if a detailed calculation for B III is carried out using this method, the result should have comparable accuracy as those for Be^+ and for Li. These data can then be used to calibrate the B spectra.

The theoretical calculations are carried out using similar basis functions and procedure as those of Davis and Chung[3] for the Be^+ systems, where multiconfiguration wave functions are employed. The main new feature in this work is the inclusion of relativistic and mass polarization corrections. For boron, the relativistic effect contributes about 0.12—0.15 eV to the binding energy of the states of interest. Hence, it should not be ignored if an accurate result is to be obtained. The relativistic effects included in this calculation are P^4, the Darwin term, and the Fermi contact term. The mass polarization effect is also considered. The Hamiltonian for B III in atomic units is given by[14]

$$H = H_0 + H_1 + H_2 + H_3 + H_4 , \tag{1}$$

where

$$H_0 = \sum_{i=1}^{3} \left(-\tfrac{1}{2}\nabla_i^2 - 5/r_i\right) + \sum_{j=1}^{3} \sum_{\substack{i=1 \\ i<j}}^{3} 1/r_{ij} , \tag{2}$$

$$H_1 = -\frac{1}{8c^2} \sum_{i=1}^{3} P_i^4 , \tag{3}$$

$$H_2 = \frac{5\pi}{2c^2} \sum_{i=1}^{3} \delta(\vec{r}_i) , \tag{4}$$

$$H_3 = -\frac{\pi}{c^2} \sum_{j=1}^{3} \sum_{\substack{i=1 \\ i<j}}^{3} \delta(\vec{r}_{ij}) - \sum_{j=1}^{3} \sum_{\substack{i=1 \\ i<j}}^{3} \frac{8\pi}{3c^2} (\vec{s}_i \cdot \vec{s}_j) \delta(\vec{r}_{ij}) , \tag{5}$$

and

$$H_4 = -a \sum_{j=1}^{3} \sum_{\substack{i=1 \\ i<j}}^{3} \vec{\nabla}_i \vec{\nabla}_j . \tag{6}$$

For ${}^5B^{11}$ the factor a is

$$a=1.008\,142/[(5\times 1.008\,142+1.008\,982\times 6)\times 1836]\ . \tag{7}$$

To assess the magnitude of the fine-structure splitting, we have also calculated the spin-orbit, spin—other-orbit, and spin-spin effects; the corresponding perturbation operators are

$$H_{\mathrm{so}}=\frac{5}{2c^2}\sum_{i=1}^{3}\frac{\vec{\mathrm{l}}_i\cdot\vec{\mathrm{s}}_i}{r_i^3}\ , \tag{8}$$

$$H_{\mathrm{soo}}=-\frac{1}{2c^2}\sum_{j=1}^{3}\sum_{\substack{i=1\\ i\neq j}}^{3}[1/r_{ij}^3(\vec{\mathrm{r}}_i-\vec{\mathrm{r}}_j)\times\vec{\mathrm{P}}_i]\cdot(\vec{\mathrm{s}}_i+2\vec{\mathrm{s}}_j)\ , \tag{9}$$

and

$$H_{\mathrm{ss}}=\sum_{\substack{i,j\\ i<j}}^{3}\frac{1}{c^2}\frac{1}{r_{ij}^3}\left[\vec{\mathrm{s}}_i\cdot\vec{\mathrm{s}}_j-\frac{3(\vec{\mathrm{s}}_i\cdot\vec{\mathrm{r}}_{ij})(\vec{\mathrm{s}}_j\cdot\vec{\mathrm{r}}_{ij})}{r_{ij}^2}\right]\ . \tag{10}$$

In Eqs. (1)—(10), $c=137.037$ which is the light velocity in atomic units. $\vec{\mathrm{l}}_i$ and $\vec{\mathrm{s}}_i$ are the orbital and spin angular momentum of the ith electron, respectively. The only part of the Breit-Pauli operator which is not included in this work is the retardation potential effect. Since it is very small for the systems of interest, i.e., of the order a few meV or less, its inclusion should not affect the result of this recalibration significantly.

The entire calculation is carried out in the LSJ scheme. For quartet states, the wave function is a simple product of spatial and spin function. For doublets, there are two different spin doublets that belong to the same eigenvalues of S^2 and S_z. The explicit expressions are given in standard quantum-mechanics textbooks.[15] Both doublets are needed in forming the total wave function. In calculating the fine structure, the good quantum number J^2,J_z is formed by coupling the proper L,S functions, i.e.,

$$|JJ_zLS\rangle=\sum_{S_z,L_z}|LSL_zS_z\rangle\langle LSL_zS_z\,|\,JJ_z\rangle\ , \tag{11}$$

where $\langle LSL_zS_z\,|\,JJ_z\rangle$ is the Clebsch-Gordan coefficient.[16]

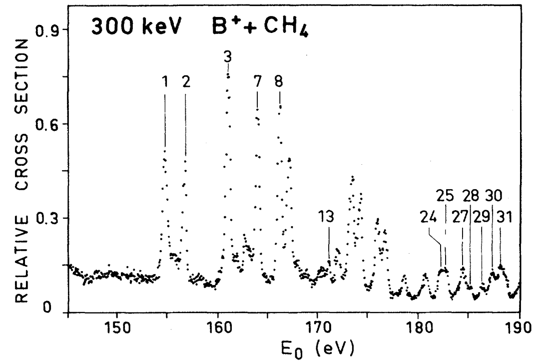

FIG. 1. High-resolution Auger-electron spectrum of boron produced by 300-keV B^+ on CH_4 at $\theta=6.4°$. Structure shown originates mainly from singly core-excited Li- and Be-like states.

The choice of angular coupling terms and the number of basis functions used are very similar to Refs. 3 and 12. Hence, these details will not be discussed here. After a few states have been calculated, it becomes clear to us that the calibration of Ref. 1 for boron is off by approximately 0.2 eV. The need for an accurate recalibration is apparent.

III. RECALIBRATION PROCEDURE

To recalibrate the spectrum a good calibration point is needed. Although $(1s2s^2)^2S$ gives a very prominent Auger peak, this line could be asymmetric, implying the peak may differ slightly from the resonance position.[17,18] In this regard, it is most ideal to use the $(1s2s2p)^4P^o$ state as the calibration point. It only couples to the continuum through relativistic interactions, i.e., spin-orbit, spin—other-orbit, and spin-spin interactions. Since J is a good quantum number and spin-spin interaction is comparatively weaker, mainly the $J=\frac{3}{2}$ and $\frac{1}{2}$ components contribute to the observed spectrum (see Fig. 1).

Our calculation shows that the splitting of these two levels is $E_{3/2}-E_{1/2}=-0.7900$ meV. It is too small to be resolved. A 12-partial-wave—80-parameter wave-function calculation gives a nonrelativistic energy of $-16.267\,391$ a.u. for the $(1s2s2p)^4P^o$ state. This is to be compared with the -16.2630 a.u. of Holøien and Geltman,[7] and $-16.267\,30$ a.u. of Larsson *et al.*[19] Larsson *et al.* used 97-term Hylleraas wave functions. Since these energy values are upper bounds to the nonrelativistic eigenvalue, our result should be considered as slightly better. These theoretical predictions are also tabulated in Table I. Re-

TABLE I. Comparison of the nonrelativistic energy and fine-structure splitting of the $(1s2s2p)^4P^o$ state in B III.

	This work	Other theories	
E_{nonrel} (a.u.)	$-16.267\,391$	$-16.267\,30$[a]	-16.2630[b]
$E_{5/2}$-$E_{3/2}$ (cm^{-1})	34.78	36.14[c]	33[d]
$E_{3/2}$-$E_{1/2}$ (cm^{-1})	-6.31	-3.21[c]	-8[d]

[a] Reference 19.

[b] Reference 7.

[c] Reference 21. This is the splitting due to relativistic effect. If the QED effects are included, the results are 36.256 and -3.194 cm^{-1}, respectively.

[d] Reference 20.

TABLE II. Calculated energies for several core-excited states of the B III ion.

	Nonrelativistic E (a.u.)	Relativistic corrections[a] (a.u.)	ΔE[b] (meV) fine-structure interval
$(1s2s2s)\,^2S$	$-16.341\,008$	$-0.005\,389$	
$(1s2s2p)\,^4P^o$	$-16.267\,391$	$-0.005\,190$	-0.7900
$[1s(2s2p)^3P]^2P^o$	$-16.106\,000$	$-0.004\,903$	$+5.002$
$[1s(2s2p)^1P]^2P^o$	$-16.000\,739$	$-0.004\,923$	-1.397
$(1s2p2p)\,^2D$	$-15.918\,753$	$-0.004\,638$	-6.872
$(1s2p2p)\,^2S$	$-15.741\,852$	$-0.004\,674$	
$[(1s2s)^3S,3s]^2S$	$-15.338\,502$	$-0.005\,098$	
$1s2s3p\,^4P$	$-15.314\,930$	$-0.005\,094$	-0.1517
$[(1s2s)^3S,3p]^2P^o$	$-15.309\,151$	$-0.005\,019$	-1.813
$[(1s2s)^3S,3d]^2D$	$-15.245\,581$	$-0.005\,029$	-0.4967
4th ^2S	$-15.220\,761$	$-0.004\,619$	
$[(1s2s)^1S,3p]^2P^o$	$-15.176\,385$	$-0.004\,661$	$+0.5256$
5th $^2P^o$	$-15.137\,089$	$-0.004\,596$	$+7.283$
$[(1s2s)^1S,3d]^2D$	$-15.116\,553$	$-0.004\,609$	$+3.578$

[a] Relativistic corrections in this calculation include P^4, the Darwin term, and the Fermi contact term as well as the mass polarization effect.

[b] $\Delta E = E(L+\frac{1}{2}) - E(L-\frac{1}{2})$ calculated from spin-orbit, spin—other-orbit, and spin-spin interaction.

cently, the fine structure of the $(1s2s2p)^4P^o$ state has been calculated by Cheng *et al.*[20] and Hata and Grant[21] using the multiconfiguration Dirac-Fock (MCDF) approach. The comparison of their result with our calculation is also given in Table I. We note that the theoretical predictions of the fine-structure splitting approximately agree with each other.

In Table II, we give the results of the calculated low-lying singly core-excited states of the B III ion. The nonrelativistic result is listed in the first column and the combined contribution of H_1, H_2, and H_3, and H_4 is given in the second column. In obtaining these results the total H in Eq. (1) is diagonalized. We note that both H_1 and H_2 give a very large contribution to the binding energy but they are opposite in sign and more than 80% of H_1 are canceled by H_2. The contribution of H_3 to the binding energy is always positive. Intuitively, this can be understood by using the following argument: It is easy to show that

$$\vec{s}_i \cdot \vec{s}_j = \frac{(\vec{s}_i + \vec{s}_j)^2}{2} - \frac{3}{4} . \tag{12}$$

If the two electrons form a triplet, then the space part of the wave function would be antisymmetric and therefore the expectation value of $\delta(\vec{r}_{ij})$ is zero. On the other hand, if $\vec{s}_i, \vec{s}_j$ forms a singlet then the first term on the right-hand side of Eq. (12) is zero and the corresponding part in H_3 becomes

$$-\pi\delta(\vec{r}_{ij}) + 2\pi\delta(\vec{r}_{ij}) = \pi\delta(\vec{r}_{ij}) \tag{13}$$

which gives a positive expectation value. This has been discussed for the two-electron system by Bethe and Salpeter.[14] For B III with a $1s^2nl$ configuration, the contribution of H_3 is about 16.3±0.5 meV. But for core-excited states, the probability of overlapping electrons is much smaller. It is of the order of 1.5 meV or less. The contribution from H_4 is about the same order of magnitude as that from H_3 for the core-excited states of B III.

In computing H_{so}, H_{soo}, and H_{ss}, we noted that the reduced matrix elements[22] for H_{soo} are negative for all the states investigated. For H_{so} most of the reduced matrix elements are positive, but there are two interesting exceptions, i.e., $[(1s2s)^3S,3p]^2P^o$ and $[(1s2s)^3S,3d]^2D$. In these cases the H_{so} contribution becomes very small. Our result contradicts some of the standard atomic physics textbooks in which the spin-orbit term has always been referred to as the largest relativistic correction by far. This statement is clearly incorrect for some of the Li-like core-excited states. This is evident by the many inverted fine-structure splittings for the doublet states in Table II. In this table, the inversion of the $(1s2s2p)^4P^o$ and $(1s2s3p)^4P^o$ are due to the combined contribution of H_{soo} and H_{ss}, but all other inversions originate from the H_{soo} contribution.

Using the results from Table II, we tabulated Auger transition energies by using the B IV $(1s^2)^1S$ energy calculated by Pekeris[23] where all relativistic effects are included. This energy is $-22.036\,908$ a.u. Since the splitting of $E_{3/2}$ and $E_{1/2}$ of $(1s2s2p)^4P^o$ is less than 1 meV, we simply take the average energy of these two substates, i.e., $-16.272\,651$ a.u. Using 1 a.u.$=27.211\,66$ eV, this gives an Auger transition energy of 156.855 eV. Comparing with unpublished experimental results of Rødbro *et al.* it appears that a shift of 0.264 eV in the energy scale is needed. The entire boron spectrum from 154 to 188 eV is then shifted by this amount. The adjusted data of the observed boron spectra are given in the last column of Table III. In Ref. 1, the positions for lines 1—8 were determined by applying a least-squares computer fitting procedure using Gaussian line shapes. The uncertainty of these centroid energies due to overlapping four-electron transitions is of

TABLE III. Recalibrated positions of the Auger spectra of boron (in eV).

Line number	Identification	Theory[a]	Reported energies[b]	Unpublished experimental results	Recalibrated position[c]
1	$(1s2s2s)\,^2S$	154.85	155.1±0.3	154.68	154.94±0.1
2	$(1s2s2p)\,^4P^o$	156.855	157.0±0.3	156.59	156.855[d]
3	$[1s(2s2p)^3P]^2P^o$	161.26	161.4±0.3	160.98	161.24±0.1
4				161.83	162.09±0.2
5				162.67	162.93±0.2
6				163.12	163.38±0.2
7	$[1s(2s2p)^1P]^2P^o$	164.12	164.3±0.5	163.86	164.12±0.1
8	$(1s2p2p)\,^2D$	166.36	165.5 ±0.5	166.12	166.38±0.1
9				167.08	167.34±0.2
10				167.93	168.19±0.2
11				168.78	169.04±0.2
12				170.31	170.57±0.2
13	$(1s2p2p)\,^2S$	171.17	171.4 ±0.7	170.99	171.25±0.2
14				171.96	172.22±0.2
15				173.32	173.58±0.2
16				174.23	174.49±0.2
17				174.57	174.83±0.2
18				175.82	176.08±0.2
19				176.62	176.88±0.2
20				177.08	177.34±0.2
21				178.50	178.76±0.2
22				180.10	180.36±0.2
23				180.67	180.93±0.2
24	$[(1s2s)^3S,3s]^2S$	182.14	182.6 ±0.7	182.16	182.42±0.2
25	$[(1s2s)^3S,3p]^2P^o$	182.94	183.0 ±0.7	182.61	182.87±0.2
26				183.82	184.08±0.2
27	$[(1s2s)^3S,3d]^2D$	184.67	184.8 ±0.7	184.39	184.65±0.2
28	4th ^2S	185.35	185.5 ±0.7	185.07	185.33±0.2
29	$[(1s2s)^1S,3p]^2P^o$	186.56	186.6 ±0.7	186.22	186.48±0.2
30	5th $^2P^o$	187.63	187.7 ±0.7	187.25	187.51±0.2
31	$[(1s2s)^1S,3d]^2D$	188.19	188.5 ±0.7	188.11	188.37±0.2

[a] Energy relative to the ground state of B IV at −22.036 908 a.u. given by Pekeris (Ref. 23) using 1 a.u. = 27.211 66 eV.

[b] Table VII of Rødbro, Bruch, and Bisgaard (Ref. 1).

[c] Lines 1—8 are fitted with a Gaussian line profile. Lines 13—31 are obtained from the maximum of computer plots.

[d] Calibration point.

the order of 0.1 eV. For the other lines an uncertainty of 0.2 eV is estimated.

IV. DISCUSSION AND CONCLUSION

If we compare the recalibrated energies with the reported experimental data in Ref. 1 (see Table VII) the new result is lower by 0.15 eV. Our calculated Auger transition energies for lithiumlike doublet states are given in the first column of Table II. Comparing these energies with the recalibrated spectrum, seven new lines can now be identified. These are labeled to be lines 24—31. It appears that all the calculated energies are lying within the experimental uncertainty quoted, except one. That is, for line 24 the calculated $[(1s2s)^3S,3s]^2S$ energy of 182.14 eV is lower than the experimental value 182.42±0.2 eV. However, we note that the spectra in the region of lines 24 and 25 are less clearly resolved; we also note that the $(1s2s3p)\,^4P^o$ state lies around 182.7 eV. Therefore, line 24 could be the result of more than one state.

In Table III we have also tabulated the recalibrated Auger lines associated with singly core-excited states in B II and B I. Very recently these states have also been calculated by Luken and Leonard.[24] Their result also supports the assignment in Table VII in Ref. 1.

In conclusion, by using a recalibration procedure we have derived very accurate experimental energies of core-excited states in boron. These results may be useful for improving isoelectronic sequence trends including relativistic corrections. Furthermore, the predicted fine-structure splitting inversion of specific core-excited states may be studied for low-Z elements by the electron beat method.[25] On the other hand, precision fine-structure measurements of medium-Z elements could be tested by high-resolution electron and photon spectroscopy. We hope that these experiments can be carried out in the near future.

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