

Isotope shifts of the three lowest 1S states of the B^+ ion calculated with a finite-nuclear-mass approach and with relativistic and quantum electrodynamics corrections

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We present very accurate quantum mechanical calculations of the three lowest S -states [$1s^22s^2(^1S_0)$, $1s^22p^2(^1S_0)$, and $1s^22s3s(^1S_0)$] of the two stable isotopes of the boron ion, $^{10}B^+$ and $^{11}B^+$. At the nonrelativistic level the calculations have been performed with the Hamiltonian that explicitly includes the finite mass of the nucleus as it was obtained by a rigorous separation of the center-of-mass motion from the laboratory frame Hamiltonian. The spatial part of the nonrelativistic wave function for each state was expanded in terms of 10 000 all-electron explicitly correlated Gaussian functions. The nonlinear parameters of the Gaussians were variationally optimized using a procedure involving the analytical energy gradient determined with respect to the nonlinear parameters. The nonrelativistic wave functions of the three states were subsequently used to calculate the leading α^2 relativistic corrections (α is the fine structure constant; $\alpha=1/c$, where c is the speed of light) and the α^3 quantum electrodynamics (QED) correction. We also estimated the α^4 QED correction by calculating its dominant component. A comparison of the experimental transition frequencies with the frequencies obtained based on the energies calculated in this work shows an excellent agreement. The discrepancy is smaller than 0.4 cm^{-1} . © 2010 American Institute of Physics. [doi:10.1063/1.3358999]

I. INTRODUCTION

A number of experimental studies of the spectrum of singly ionized boron, B II, has been recently undertaken.^{1,2} The initial motivation for the study was the search for the “missing” $2s3s\ ^1S$ term. It took a number of attempts during nearly three decades to finally identify this level in the spectrum. Even though the energy of this term had been fairly well predicted in 1973 by Weiss (see Ref. 2), a large discrepancy persisted for a long time between Weiss’ value and the earlier known experimental value. This was despite the theory and experiment agreeing within $100\text{--}200\text{ cm}^{-1}$ for other B II levels. The disagreement between the theory and experiment of the $2s3s\ ^1S$ level stimulated several experimental studies from beam-foil experiments to high-resolution spark spectroscopy, as well as more refined theoretical calculations. In the course of these studies not only the missing $2s3s\ ^1S$ level of B II was finally discovered, but also new spectral information on this ion has been collected that included more than 80 newly classified (or revised) spectral lines.¹ In effect, B II has become one of the best studied small singly charged atomic ions.

The purpose of this study is to describe the three lowest 1S states (including the $2s3s\ ^1S$ state) of two stable B II isotopes, $^{10}B^+$ and $^{11}B^+$, with the highest possible accuracy of the quantum mechanical calculations. This involves varia-

tional nonrelativistic calculations performed with all-electron explicitly correlated Gaussian (ECG) basis functions followed by perturbation theory calculations of the leading relativistic and quantum electrodynamics (QED) corrections. Up to 10 000 ECGs have been used for each state. In recent works^{3–7} we have shown that the ECG basis functions are an excellent tool for performing very accurate calculations for ground and excited states of small atoms and that the calculations on atoms with four to five electrons can be nearly as accurate as for three-electron atoms. These later systems have been studied by several groups using Hylleraas basis functions,^{8–12} which better represent the wave function in the cusp region, but so far their use has not been extended beyond three electron atoms.

To reach high accuracy in the calculations we used an approach that explicitly includes the coupling between the motion of the electrons and the motion of the nucleus in the nonrelativistic variational calculations. This finite-nuclear-mass (FNM) approach, which treats the electrons and the nucleus on equal footing, requires that the wave function of the system used in the calculations depends on the coordinates of the electrons and the nucleus. The FNM approach enables direct determination of the shifts of the energy levels of the B^+ ion due to the difference in the nuclear masses of the $^{10}B^+$ and $^{11}B^+$ isotopes.

To best represent the electron-electron and nucleus-electron correlation effects in the wave function, it needs to

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be expanded in terms of basis functions that explicitly depend on the interparticle distances (i.e., the distances between electrons and the distances between the electrons and the nucleus). All-particle ECGs are such functions. The advantage of using ECGs in atomic calculations is related to the fact that the Hamiltonian matrix elements with these functions, as well as the matrix elements involved in calculating the relativistic and QED corrections, are manageable and can be expressed with relatively simple and compact formulas for an arbitrary number of particles. However, the Gaussians do not satisfy the electron-electron and electron-nucleus cusp conditions and are somewhat inefficient in describing the long-range behavior of the wave function. These drawbacks are usually largely overcome by the use of longer expansions of the wave functions in terms of Gaussians.

As the aim of the present calculation was to reach the spectroscopic accuracy for the transition energies, thousands of ECGs in the wave function expansion were needed. This puts high demands on the computer resources. When one uses all-electron ECGs the computation time required for a single point energy calculations (single point in the space of nonlinear parameters) scales as $c_1 \times n! \times n^4 \times K^2 + c_2 \times K^3$, where c_1 and c_2 are some constants, K is the number of basis functions, and n is the number of electrons in the system. The $n!$ dependence results from the number of the permutations that need to be applied to the total wave function to make it antisymmetric with respect to permutations of the electron labels. The K^3 term is due to solving the generalized eigenvalue problem with dense overlap and Hamiltonian matrices. While for very large basis sets this term will eventually dominate, in calculations on systems containing more than two electrons with a few thousand basis functions it usually accounts only for relatively small amount of the total calculation time. A significantly larger amount of time is spent on computing the matrix elements.

A key feature of very accurate variational calculations with ECGs is the optimization of the exponential parameters of the Gaussians. In our atomic calculations the optimization is performed with the procedure that utilizes analytical derivatives of the energy with respect to the Gaussian exponential parameters.^{13–15} The derivatives form the gradient vector. Its elements depend on the derivatives of the Hamiltonian and overlap matrix elements. During the variational optimization the energy and the gradient are calculated millions of times and it is essential that this part of the calculation is efficiently parallelized. The availability of the analytic gradient considerably accelerates the calculation and is the key to achieving high accuracy.

As the state-of-the-art experiments on atomic spectra now reach the relative accuracy of 10^{-8} – 10^{-9} , matching this accuracy with first-principles calculations represents a considerable challenge. In this work we show that the calculations with ECGs can step up to this challenge.

Three steps have been involved in the present calculations. The first, the most time consuming one, was the variational calculation of the nonrelativistic wave function and the corresponding energy for each considered state. The second step involved the calculation of the leading α^2 relativistic corrections. In the third step, which was also time consum-

ing, the α^3 and α^4 QED corrections were calculated in the framework of the nonrelativistic QED method and the perturbation theory^{16–18} with the zeroth-order level being the nonrelativistic Schrödinger equation.

The questions this work attempts to answer are the following. (1) How accurately is the state-of-the-art theoretical method which includes FNM effects, first order relativistic corrections, and the leading QED corrections able to describe the lowest 1S states (particularly the $1s^2 2s 3s$ 1S state) of the B^+ ion? This question is particularly relevant with regards to the relativistic correction, which grows quite rapidly as the nuclear charge increases and the model based on calculating this correction at the first order level may start to fail. (2) How big are the shifts of the transition energies for the lowest 1S states due to the nuclear-mass effect and are those shifts large enough to be measured experimentally?

II. THE METHOD

In the nonrelativistic variational calculations we use the following Hamiltonian:

$$\hat{H}_{\text{int}} = -\frac{1}{2} \left(\sum_{i=1}^4 \frac{1}{\mu_i} \nabla_{\mathbf{r}_i}^2 + \sum_{i=1}^4 \sum_{j \neq i}^4 \frac{1}{m_0} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} \right) + \sum_{i=1}^4 \frac{q_0 q_i}{r_i} + \sum_{i=1}^4 \sum_{i < j}^4 \frac{q_i q_j}{r_{ij}}, \quad (1)$$

where in atomic units $q_0=5$ (the charge of the nucleus), $q_1=q_2=q_3=q_4=-1$ (the charges of the electrons), $m_0=20\,063.737\,52$ for the ^{11}B nucleus or $m_0=18\,247.468$ for the ^{10}B nucleus, μ_i are the reduced electron masses, $\mu_i = m_0 m_i / (m_0 + m_i)$, where $m_1=m_2=m_3=m_4=1$, \mathbf{r}_i , $i=1, 2, 3, 4$, are the position vectors of the electrons with respect to the nucleus, r_i are their lengths, and $r_{ij}=|\mathbf{r}_j-\mathbf{r}_i|$ are the distances between the electrons. The Hamiltonian (1) is obtained by rigorously separating the center-of-mass motion from the nonrelativistic laboratory frame Hamiltonian.^{14,19} This separation reduces the five-particle problem of the B^+ ion to a four “pseudoparticle” problem. The calculations have been carried out for finite masses of the B nucleus, as well as for infinite nuclear mass. They yielded the nonrelativistic energies, E_{nonrel} , and the corresponding wave functions. The infinite nuclear mass results were generated to serve as a reference for calculations performed by others in the framework of the Born–Oppenheimer approximation.

Denoting by \mathbf{r} the 12×1 vector of the internal Cartesian electron coordinates, $\mathbf{r}=(\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}'_3, \mathbf{r}'_4)'$ (the prime symbol denotes the vector/matrix transposition) and by σ the spin coordinates of the electrons and the nucleus we can write the complete wave function of B^+ as

$$\Psi(\mathbf{r}, \sigma) = \hat{A}[\Phi(\mathbf{r})\Omega_{S,M_S}(\sigma)]. \quad (2)$$

\hat{A} antisymmetrizes the electron labels and $\Omega_{S,M_S}(\sigma)$ is a product of the spin functions of the electrons and the nucleus, $\Omega_{S,M_S} = \Omega^e \Omega^N$. For the states considered in this work Ω^e represents a four-electron singlet spin function. In practical calculations it is more convenient to use the spin-free formalism.^{20,21} In that formalism only the spatial wave func-

TABLE I. Variational nonrelativistic energies, leading relativistic corrections, and the total energies, $E_{\text{tot}}=E_{\text{nonrel}}+\alpha^2(\langle H_{\text{MV}} \rangle+\langle H_{\text{D}} \rangle+\langle H_{\text{SS}} \rangle+\langle H_{\text{OO}} \rangle)$. All numbers are in a.u. Values in parentheses are estimates of the remaining uncertainty.

System	State	Basis size	E_{nonrel}	$\langle H_{\text{MV}} \rangle$	$\langle H_{\text{D}} \rangle$	$\langle H_{\text{SS}} \rangle$	$\langle H_{\text{OO}} \rangle$	$E_{\text{nonrel}}+\alpha^2 E_{\text{rel}}$
[∞] B ⁺	2 ¹ S ₀	7000	-24.348 884 425	-699.7921	558.1768	22.4857	-1.5126	-24.355 308 784
		8000	-24.348 884 433	-699.7972	558.1813	22.4856	-1.5126	-24.355 308 837
		9000	-24.348 884 439	-699.7972	558.1816	22.4855	-1.5126	-24.355 308 830
		10 000	-24.348 884 444	-699.7972	558.1816	22.4855	-1.5126	-24.355 308 830
		10 000 ^a	-24.348 884 446(35)	-699.7972	558.1816	22.4855	-1.5126	-24.355 308 833(100)
	3 ¹ S ₀	7000	-23.767 561 721	-670.2321	537.0833	21.2197	-0.5977	-23.773 553 920
		8000	-23.767 561 771	-670.2346	537.0889	21.2196	-0.5977	-23.773 553 809
		9000	-23.767 561 802	-670.2341	537.0899	21.2196	-0.5977	-23.773 553 765
		10 000	-23.767 561 826	-670.2460	537.1015	21.2194	-0.5977	-23.773 553 820
		10 000 ^a	-23.767 561 866(60)	-670.2457	537.1012	21.2194	-0.5977	-23.773 553 855(400)
	4 ¹ S ₀	7000	-23.722 007 222	-684.1310	547.4189	21.7720	-1.2747	-23.728 195 821
		8000	-23.722 007 265	-684.1424	547.4320	21.7716	-1.2747	-23.728 195 792
		9000	-23.722 007 294	-684.1699	547.4580	21.7714	-1.2747	-23.728 195 913
		10 000	-23.722 007 316	-684.1738	547.4612	21.7713	-1.2747	-23.728 195 978
		10 000 ^a	-23.722 007 330(100)	-684.1738	547.4612	21.7713	-1.2747	-23.728 195 995(250)
¹¹ B ⁺	2 ¹ S ₀	7000	-24.347 641 267	-699.6505	558.0921	22.4827	-1.5691	-24.354 065 761
		8000	-24.347 641 275	-699.6556	558.0966	22.4826	-1.5691	-24.354 065 813
		9000	-24.347 641 281	-699.6556	558.0969	22.4825	-1.5691	-24.354 065 807
		10 000	-24.347 641 286	-699.6555	558.0969	22.4825	-1.5691	-24.354 065 806
		10 000 ^a	-24.347 641 289(35)	-699.6555	558.0969	22.4825	-1.5691	-24.354 065 809(100)
	3 ¹ S ₀	7000	-23.766 371 888	-670.0886	536.9957	21.2166	-0.6508	-23.772 364 107
		8000	-23.766 371 938	-670.0911	537.0014	21.2165	-0.6508	-23.772 363 996
		9000	-23.766 371 969	-670.0906	537.0024	21.2164	-0.6508	-23.772 363 952
		10 000	-23.766 371 993	-670.1026	537.0139	21.2163	-0.6508	-23.772 364 007
		10 000 ^a	-23.766 372 033(60)	-670.1023	537.0136	21.2163	-0.6508	-23.772 364 042(400)
	4 ¹ S ₀	7000	-23.720 807 259	-684.0006	547.3417	21.7694	-1.3302	-23.726 996 110
		8000	-23.720 807 302	-684.0119	547.3548	21.7690	-1.3302	-23.726 996 081
		9000	-23.720 807 332	-684.0395	547.3808	21.7688	-1.3302	-23.726 996 202
		10 000	-23.720 807 353	-684.0433	547.3840	21.7687	-1.3302	-23.726 996 267
		10 000 ^a	-23.720 807 367(100)	-684.0434	547.3840	21.7687	-1.3302	-23.726 996 285(250)
¹⁰ B ⁺	2 ¹ S ₀	7000	-24.347 517 538	-699.6364	558.0837	22.4824	-1.5747	-24.353 942 045
		8000	-24.347 517 546	-699.6415	558.0881	22.4823	-1.5747	-24.353 942 097
		9000	-24.347 517 552	-699.6415	558.0884	22.4822	-1.5747	-24.353 942 091
		10 000	-24.347 517 557	-699.6414	558.0885	22.4822	-1.5747	-24.353 942 090
		10 000 ^a	-24.347 517 559(35)	-699.6414	558.0885	22.4822	-1.5747	-24.353 942 093(100)
	3 ¹ S ₀	7000	-23.766 253 467	-670.0743	536.9870	21.2163	-0.6561	-23.772 245 688
		8000	-23.766 253 517	-670.0768	536.9926	21.2162	-0.6561	-23.772 245 577
		9000	-23.766 253 548	-670.0764	536.9936	21.2161	-0.6561	-23.772 245 533
		10 000	-23.766 253 571	-670.0883	537.0052	21.2159	-0.6561	-23.772 245 587
		10 000 ^a	-23.766 253 612(60)	-670.0880	537.0049	21.2160	-0.6561	-23.772 245 623(400)
	4 ¹ S ₀	7000	-23.720 687 828	-683.9876	547.3340	21.7691	-1.3357	-23.726 876 705
		8000	-23.720 687 871	-683.9989	547.3471	21.7688	-1.3357	-23.726 876 675
		9000	-23.720 687 901	-684.0265	547.3731	21.7686	-1.3357	-23.726 876 796
		10 000	-23.720 687 922	-684.0304	547.3763	21.7684	-1.3357	-23.726 876 861
		10 000 ^a	-23.720 687 936(100)	-684.0304	547.3763	21.7684	-1.3357	-23.726 876 879(250)

^aResults obtained after several additional optimization cycles.

tion, $\Phi(\mathbf{r})$, enters the calculation. However, before it is used, $\Phi(\mathbf{r})$ has to be transformed with the appropriate Young operator that represents the permutational symmetry properties of the state under consideration.

The following S -Gaussians were used to expand the spatial wave functions, $\Phi(\mathbf{r})$, for the three ¹S₀ states considered in the present calculations:

$$\phi_k = \exp[-\mathbf{r}'(L_k L_k' \otimes I_3)\mathbf{r}], \quad (3)$$

where \otimes is the Kronecker product symbol, L_k is a 4×4 lower triangular matrix of nonlinear variational parameters,

and I_3 is the 3×3 identity matrix. The Cholesky factored form representation, $L_k L_k'$, of the matrix of the Gaussian exponential parameters ensures the square integrability of ϕ_k for any values of the L_k matrix elements. This is important in the optimization of these parameters because it can be carried out without any restrictions [i.e., the L_k matrix elements can be varied in the range of $(-\infty, +\infty)$], which makes the optimization much more efficient.

The variational optimization of trial wave functions performed in the present calculations has been done independently for each state. As it was already mentioned, in the

TABLE II. Convergence of nonrelativistic and relativistic transition energies for ${}^{\infty}\text{B}^+$, ${}^{11}\text{B}^+$, and ${}^{10}\text{B}^+$. All values are in cm^{-1} .

Transition	Basis size	${}^{\infty}\text{B}^+$, nonrel	${}^{\infty}\text{B}^+$, rel	${}^{11}\text{B}^+$, nonrel	${}^{11}\text{B}^+$, rel	${}^{10}\text{B}^+$, nonrel	${}^{10}\text{B}^+$, rel
$2\ ^1S_0 \rightarrow 3\ ^1S_0$	5000	127 585.626	127 680.513	127 573.922	127 668.834	127 572.757	127 667.671
	6000	127 585.600	127 680.435	127 573.896	127 668.757	127 572.731	127 667.594
	7000	127 585.586	127 680.434	127 573.883	127 668.756	127 572.718	127 667.593
	8000	127 585.577	127 680.470	127 573.873	127 668.792	127 572.708	127 667.629
	9000	127 585.571	127 680.478	127 573.868	127 668.800	127 572.703	127 667.638
	10 000	127 585.567	127 680.466	127 573.864	127 668.788	127 572.699	127 667.626
	10 000*	127 585.559(15)	127 680.459(60)	127 573.855(15)	127 668.781(60)	127 572.691(15)	127 667.618(60)
Experiment					127 661.19		
$2\ ^1S_0 \rightarrow 4\ ^1S_0$	5000	137 583.675	137 635.425	137 574.195	137 625.919	137 573.251	137 624.973
	6000	137 583.655	137 635.431	137 574.174	137 625.925	137 573.231	137 624.979
	7000	137 583.643	137 635.387	137 574.163	137 625.880	137 573.219	137 624.934
	8000	137 583.635	137 635.404	137 574.155	137 625.898	137 573.212	137 624.952
	9000	137 583.630	137 635.376	137 574.150	137 625.870	137 573.207	137 624.924
	10 000	137 583.627	137 635.362	137 574.146	137 625.856	137 573.203	137 624.910
	10 000*	137 583.624(20)	137 635.359(75)	137 574.144(20)	137 625.853(75)	137 573.201(20)	137 624.907(75)
Experiment					137 622.25		

energy minimization we employed the analytic gradient with respect to the L_k matrix elements,^{13–15} which significantly accelerates the optimization process and reduces its computational cost. Without the use of the analytic gradient the present calculations could not be performed at the accuracy level achieved in this work.

The calculations of the relativistic effects have been performed as the expectation value of the Dirac–Breit Hamiltonian in the Pauli approximation (\hat{H}_{rel})^{22,23} transformed to the internal coordinate system. For the states with the S symmetry considered in this work \hat{H}_{rel} includes the mass-velocity (MV), Darwin (D), orbit-orbit (OO), and spin-spin (SS) terms:

$$\hat{H}_{\text{rel}} = \hat{H}_{\text{MV}} + \hat{H}_{\text{D}} + \hat{H}_{\text{OO}} + \hat{H}_{\text{SS}}. \quad (4)$$

In the internal coordinates these operators are

$$\hat{H}_{\text{MV}} = -\frac{1}{8} \left[\frac{1}{m_0^3} \left(\sum_{i=1}^4 \nabla_{\mathbf{r}_i} \right)^4 + \sum_{i=1}^4 \frac{1}{m_i^3} \nabla_{\mathbf{r}_i}^4 \right], \quad (5)$$

$$\hat{H}_{\text{D}} = -\frac{1}{2} \pi \left[\sum_{i=1}^4 \frac{q_0 q_i}{m_i^2} \delta^3(\mathbf{r}_i) + \sum_{i=1}^4 \sum_{j \neq i}^4 \frac{q_i q_j}{m_i^2} \delta^3(\mathbf{r}_{ij}) \right], \quad (6)$$

$$\begin{aligned} \hat{H}_{\text{OO}} = & -\frac{1}{2} \sum_{i=1}^4 \sum_{j=1}^4 \frac{q_0 q_i}{m_0 m_i} \left[\frac{1}{r_i} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} + \frac{1}{r_i^3} \mathbf{r}_i \cdot (\mathbf{r}_i \cdot \nabla_{\mathbf{r}_i}) \nabla_{\mathbf{r}_j} \right] \\ & + \frac{1}{2} \sum_{i=1}^4 \sum_{j>i}^4 \frac{q_i q_j}{m_i m_j} \left[\frac{1}{r_{ij}} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} \right. \\ & \left. + \frac{1}{r_{ij}^3} \mathbf{r}_{ij} \cdot (\mathbf{r}_{ij} \cdot \nabla_{\mathbf{r}_i}) \nabla_{\mathbf{r}_j} \right], \quad (7) \end{aligned}$$

$$\hat{H}_{\text{SS}} = -\frac{2}{3} \pi \sum_{i=1}^4 \sum_{j>i}^4 \frac{q_i q_j}{m_i m_j} \delta^3(\mathbf{r}_{ij}) (\mathbf{s}_i \cdot \mathbf{s}_j). \quad (8)$$

In the present calculations we have not included the magnetic anomaly factors for the electrons and the nucleus in the

Darwin and spin-spin corrections. The relativistic correction calculations have been performed for the finite and infinite masses of the B nucleus. Thus the value of the correction varies with the nuclear mass.

In calculating the leading QED corrections of the order α^3 and α^4 (called here E_{QED} and E_{HQED} , respectively) in this work we used the approach described by Pachucki *et al.*^{24–27} The approach is based on the perturbation theory employed in the framework of the nonrelativistic QED method.^{16–18} The zeroth-order level in this approach is the nonrelativistic Schrödinger equation. The algorithm used here was also employed in our recent work on the ground and excited states of the Be atom.⁶ The α^3 and α^4 QED corrections represent the two-photon exchange, the vacuum polarization, and the electron self-energy effects. The most difficult terms to calculate in the α^3 correction are the Araki–Sucher term ($\langle (P(1/r_{ij}^3)) \rangle / (4\pi)$) and the Bethe logarithm ($\ln k_0$). It should be emphasized that for the QED correction of the order α^4 we only determined the dominant contribution, which is the simplest to calculate. As the procedure used in this work for calculating the α^3 and α^4 QED corrections was only developed for the infinite-mass case only this type of calculations have been performed.

The numerical values of the fine structure constant and the Hartree-wavenumber conversion factor used in this work were taken from Ref. 28. They are $\alpha = 7.297\,352\,537\,6 \times 10^{-3}$, $1 \text{ hartree} = 2.194\,746\,313\,705 \times 10^5 \text{ cm}^{-1}$.

III. RESULTS

First, the variational nonrelativistic FNM calculations have been performed for each of the three considered states ($1s^2 2s^2\ ^1S_0$, $1s^2 2p^2\ ^1S_0$, and $1s^2 2s 3s\ ^1S_0$) of the most dominant ${}^{11}\text{B}^+$ isotope. In the calculations the basis set for each state has been grown to the size of 10 000 functions. The growing of the basis set involved gradually adding subsets of 20 functions to the basis set and optimizing each function of the subset with the gradient-based energy minimization procedure, one function at a time. After the addition of each

TABLE III. The Araki–Sucher term and the Bethe logarithm as well as the total α^3 and α^4 QED corrections ($\alpha^3 E_{\text{QED}}$ and $\alpha^4 E_{\text{HQED}}$) obtained in the infinite-mass calculations with 10 000-term ground state wave function. All values are in a.u.

State	$\langle P(1/r_{ij}^3) \rangle / (4\pi)$	$\ln k_0$	$\alpha^3 E_{\text{QED}}$	$\alpha^4 E_{\text{HQED}}$
2^1S_0	-2.344 317(1)	6.1944(9)	$7.913\ 612\ 8(4) \times 10^{-4}$	$4.944\ 00 \times 10^{-5}$
3^1S_0	-2.103 286(3)	6.1991(8)	$7.604\ 072(2) \times 10^{-4}$	$4.755\ 71 \times 10^{-5}$
4^1S_0	-2.277 398(6)	6.1969(8)	$7.756\ 976(7) \times 10^{-4}$	$4.847\ 95 \times 10^{-5}$

20 functions the entire basis set was reoptimized in a cyclic optimization where again the parameters of one function at a time were reoptimized. In adding new functions to the basis set a stochastic procedure was used.^{29,30} In this procedure new basis functions are selected from a set of candidates, which are generated stochastically based on the distributions of nonlinear parameters of already included basis functions. When the candidate that minimizes the energy the most is added to the basis, its nonlinear parameters are further tuned using the analytic gradient. When the basis size of 10 000 functions was reached for each state, several additional cyclic optimizations were performed of all the functions to generate the final basis set. Next, the basis sets generated for the $^{11}\text{B}^+$ isotope were used to calculate the energies of the three states of the $^{10}\text{B}^+$ isotope, as well as of the boron ion with an infinite nuclear mass $^\infty\text{B}^+$. As the change in the wave function caused by the change of the nuclear mass is small (which is true as long as the mass of the nucleus remains much larger than the mass of the electron), it is sufficient to adjust only the linear coefficients of the basis functions without reoptimizing the nonlinear parameters. The nonrelativistic energies resulted from the calculations are shown in Table I.

The next step involved the calculations of the α^2 relativistic corrections, i.e., the mass-velocity, Darwin, spin-spin interaction, and orbit-orbit corrections. In Table I we show how these corrections converge with the number of basis functions for $^{10}\text{B}^+$, $^{11}\text{B}^+$, and $^\infty\text{B}^+$. We also show the total energies that include the relativistic corrections. The convergence of the transition energies calculated as the differences of the nonrelativistic and relativistic total energies taken from Table I are presented in Table II.

In the next step of the calculations the leading α^3 and α^4 QED corrections were determined. The results are presented in Table III. Apart from the values of the corrections we also show in the table the values of the Araki–Sucher term and

the Bethe logarithm, which, as mentioned, are the most difficult to compute. For the discussion on the accuracy of the procedure to calculate the QED corrections we refer the reader to the work in Ref. 27.

The last step involved calculating the energies corresponding to the transitions between the considered three states for the two B⁺ isotopes and for $^\infty\text{B}^+$. The transition energies are presented in Table IV. For each value we show the numerical uncertainty determined based on the level of the convergence of the particular value with the number of basis functions and on other factors contributing to the numerical noise in the calculations. In the case of $E_{\text{QED}}^{(4)}$ the uncertainty is mainly due to the approximate treatment of that correction used in this work rather than the finite size of the basis. In the table we also show the experimental transition energies taken from Refs. 1 and 2.

Upon an analysis of the results obtained for $^{11}\text{B}^+$ shown in Table IV, one can see that, after adding all the contributions, the calculated transition energies are within 0.4 cm⁻¹ of the experimental transitions. The agreement is somewhat better for the $2^1S_0 \rightarrow 4^1S_0$ transition [the calculated 137 622.204(175) cm⁻¹ versus the experimental 137 622.25 cm⁻¹] than for the $2^1S_0 \rightarrow 3^1S_0$ transition [127 661.574(260) cm⁻¹ versus 127 661.19 cm⁻¹]. It is likely that including the missing term of the $E_{\text{QED}}^{(4)}$ correction will improve the agreement even further. The results for $^{10}\text{B}^+$, which are also shown in Table IV, should have a similar accuracy as the $^{11}\text{B}^+$ results. They allow to estimate the isotope shifts of the two calculated transitions. The $^{11}\text{B}^+ \rightarrow ^{10}\text{B}^+$ shift for the $2^1S_0 \rightarrow 3^1S_0$ transition is -1.163 cm⁻¹ and for the $2^1S_0 \rightarrow 4^1S_0$ transition it is 0.946 cm⁻¹. Both shifts are large enough to be determined experimentally.

IV. SUMMARY

All-electron ECG functions have been employed to perform very accurate calculations of the three lowest *S* states and the corresponding transition energies of the boron singly charged cation assuming finite nuclear mass. The calculations also included the leading relativistic and QED corrections. The calculated transition energies obtained for the $^{11}\text{B}^+$ isotope agree with the experimental values within 0.4 cm⁻¹. The calculations also yielded shifts of the transition energies due to the $^{11}\text{B}^+ \rightarrow ^{10}\text{B}^+$ isotope substitution, which are large enough to be verified experimentally. The calculations presented in this work are by far the most accurate ever per-

TABLE IV. Convergence of the $2^1S_0 \rightarrow 3^1S_0$ and $2^1S_0 \rightarrow 4^1S_0$ transition energies for $^\infty\text{B}^+$, $^{11}\text{B}^+$, and $^{10}\text{B}^+$ with the inclusion of increasingly higher level correction (finite-mass, relativistic, and QED) to the energies of the three states. All values are in cm⁻¹.

Contribution included	$^\infty\text{B}^+$		$^{11}\text{B}^+$		$^{10}\text{B}^+$	
	$2^1S_0 \rightarrow 3^1S_0$	$2^1S_0 \rightarrow 4^1S_0$	$2^1S_0 \rightarrow 3^1S_0$	$2^1S_0 \rightarrow 4^1S_0$	$2^1S_0 \rightarrow 3^1S_0$	$2^1S_0 \rightarrow 4^1S_0$
$E_{\text{nonrel}} (M_{\text{nucl}} = \infty)$	127 585.559(15)	137 583.624(20)	127 585.559(15)	137 583.624(20)	127 585.559(15)	137 583.624(20)
$E_{\text{nonrel}} (\text{finite nucl. mass})$	127 585.559(15)	137 583.624(20)	127 573.855(15)	137 574.144(20)	127 572.691(15)	137 573.201(20)
E_{rel}	127 680.459(60)	137 635.359(75)	127 668.781(60)	137 625.853(75)	127 667.618(60)	137 624.907(75)
$E_{\text{QED}}^{(3)}$	127 673.666(60)	137 631.921(75)	127 661.987(60)	137 622.415(75)	127 660.825(60)	137 621.469(75)
$E_{\text{QED}}^{(4)}$	127 673.252(260)	137 631.710(175)	127 661.574(260)	137 622.204(175)	127 660.411(260)	137 621.258(175)
Experiment			127 661.19	137 622.25		

formed for the three 1S states of the boron ion. They show that the nonrelativistic QED method provides a very accurate framework for atomic calculations even for systems with heavier nuclei.

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