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# Lowest ${}^2S$ electronic excitations of the boron atom.

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A theoretical *ab-initio* approach for calculating bound states of small atoms is developed and implemented. The approach is based on finite-nuclear-mass (non-Born-Oppenheimer; non-BO) non-relativistic variational calculations performed with all-particle explicitly correlated Gaussian functions and includes the leading relativistic and quantum electrodynamics (QED) energy corrections determined using the non-BO wave functions. The approach is applied to determine the total and transition energies for the lowest four  ${}^2S$  electronic excitations of the boron atom. The transition energies agree with the available experimental values within  $0.2\text{--}0.3\text{ cm}^{-1}$ . Previously such accuracy was achieved for three- and four-electron systems.

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The calculation of atomic energy levels and transition frequencies with the spectroscopic precision remains one of the most formidable problems since the early days of quantum theory. The main challenge is to overcome the rapid exponential growth in the amount of computations with the increase in the system size (number of electrons), while retaining the high accuracy in the calculations. In the past several decades many successful quantum-chemical approaches have been developed that brought dramatic advances to the electronic structure theory and open up ways for numerous applications. However, many of these methods are only capable of reaching the chemical accuracy (of the order of 1 kcal/mol) and often cannot effectively deal with excited states.

The problem of precise determination of the atomic energies and other basic properties stems not only from the strong interaction between the particles, but also from more subtle effects due to relativism, QED, and finite nuclear mass and size. Until about a decade ago the largest system that could be treated at the truly spectroscopic level of accuracy was the lithium atom [1, 2]. In 2006-2007 there were works [3, 4] on the lowest excitation energy of the beryllium atom that employed all-electron explicitly correlated Gaussian functions (ECGs). The obtained value for the  $3^1S \rightarrow 2^1S$  transition energy in these works was within the experimental error bar from the value obtained in the experiment by Johansson [5, 6].

In this Letter we report on a next step in the journey towards precision calculations of the ground and excited states of small fully-correlated state-of-the-art calculations of five-electron systems can now be performed with similar accuracy as achieved previously for He, Li, and Be.

There have been some high-accuracy calculations concerning boron ground and excited states before. In 2011 we presented calculations performed for the two lowest  ${}^2P$  and the lowest  ${}^2S$  states of boron performed with 5100 ECGs [7]. In 2015 Puchalski *et al.* [8] also calcu-

lated the boron ground  ${}^2P$  state and the first excited  ${}^2S$  state using 8192 ECGs. Their calculations included the leading relativistic and QED corrections.

Since the work on Be [4] was published, several important upgrades have been implemented in the theoretical approach used in the calculations. The Araki-Sucher and Kabir-Salpeter terms, which appear in the QED correction, have also been implemented in the non-BO approach. The computer code has been made more efficient in terms of the parallel performance. Also, a regularization approach (which we call “drachmanization” [9, 10]) has been implemented in the calculation of certain expectation values with the non-BO wave functions. The new approach now allows for performing calculations on a five-electron atom with a similar accuracy as achieved in our Be calculations done in 2007. The present work concerning the lowest four excited  ${}^2S$  states of the boron atom (i.e. states  $3^1S$ ,  $4^1S$ ,  $5^1S$ , and  $6^1S$ ) is the first in a series studies concerning five-electron systems that demonstrates this new capability.

In recent years various types of ECG basis functions have been used in very accurate variational atomic and molecular calculations performed with an approach where the BO approximation is not assumed [11–13]. In this approach, the motion of the electrons is treated on equal footing with the motion of the nuclei. With that effects due to the finite nuclear mass such as isotope shifts of the spectral transitions, relativistic recoil effects, etc., can be directly determined without resorting to the perturbation theory.

The advantage of using ECGs in atomic and molecular calculations over other types of explicitly correlated functions, such as Slaters or Hylleraas-type functions [14–18], is due to the ease in calculating the multiparticle matrix elements with them. Moreover, the expression for the total energy obtained using ECGs can be easily analytically differentiated with respect to the Gaussian exponential parameters and the energy gradient can be determined.

The use of the analytic gradient is crucially important as it allows for very efficient variational optimization of the wave function, which is necessary to achieve high accuracy in the calculations.

$^{10}\text{B}$  and  $^{11}\text{B}$  atoms are six-particle systems each consisting of five electrons and a nucleus. After separating out the motion of the center of mass [12], the six-particle problem is reduced to an effective five-particle problem. The resulting internal nonrelativistic Hamiltonian,  $H_{\text{nr}}$ , for the boron atom has the following form in atomic units (a.u.):

$$H_{\text{nr}} = -\frac{1}{2} \left( \sum_{i=1}^5 \frac{1}{\mu_i} \nabla_{\mathbf{r}_i}^2 + \sum_{i=1}^5 \sum_{j \neq i}^5 \frac{1}{m_1} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} \right) + \sum_{i=1}^5 \frac{q_0 q_i}{r_i} + \sum_{i=1}^5 \sum_{j < i}^5 \frac{q_i q_j}{r_{ij}}, \quad (1)$$

where  $q_0 = +5$  is the nuclear charge,  $q_i = -1$ ,  $i = 1, \dots, 5$  are charges of the electrons,  $m_0$  is the mass of the nucleus (we used  $m_0 = 18247.46879$  a.u. for  $^{10}\text{B}$  and  $m_0 = 20063.73729$  a.u. for  $^{11}\text{B}$ ),  $m_i = 1$ ,  $i = 1, \dots, 5$  are the electron masses, and  $\mu_i = m_0 m_i / (m_0 + m_i)$ ,  $i = 1, \dots, 5$  are the reduced masses of the electrons. The separation of the internal Hamiltonian and the Hamiltonian of the motion of the center of mass is rigorous. The mass-polarization term and reduced masses  $\mu_i$  describe the effect of a finite nuclear mass in a non-perturbative way.

For light atoms the most practical approach to account for relativistic and QED effects is to expand the total energy in powers of the fine structure constant [19, 20],

$$E_{\text{tot}} = E_{\text{nr}} + \alpha^2 E_{\text{rel}}^{(2)} + \alpha^3 E_{\text{QED}}^{(3)} + \alpha^4 E_{\text{HQED}}^{(4)} \dots,$$

where  $E_{\text{nr}}$  is an eigenvalue of the nonrelativistic Hamiltonian (1),  $\alpha^2 E_{\text{rel}}^{(2)}$  includes the leading relativistic correction, and  $\alpha^3 E_{\text{QED}}^{(3)}$  and  $\alpha^4 E_{\text{HQED}}^{(4)}$  represent the leading and higher order QED corrections, respectively.

Quantities  $E_{\text{rel}}^{(2)}$ ,  $E_{\text{QED}}^{(3)}$ , and others can be evaluated in the framework of the perturbation theory using the non-BO nonrelativistic wave function corresponding to  $E_{\text{nr}}$  as the zero-order solution. They represent the expectation values of some effective Hamiltonians. In this work  $E_{\text{rel}}^{(2)}$  corresponds to the Dirac–Breit Hamiltonian in the Pauli approximation [21, 22]. In the case of  $S$ -states this Hamiltonian contains the following contributing terms,

$$H_{\text{rel}}^{(2)} = H_{\text{MV}} + H_{\text{D}} + H_{\text{OO}} + H_{\text{SS}}, \quad (2)$$

traditionally referred to as the mass–velocity, Darwin, orbit–orbit, and spin–spin terms. In the internal coordi-

nates their explicit form is given by [12]:

$$\begin{aligned} H_{\text{MV}} &= -\frac{1}{8} \left( \frac{1}{m_0^3} \left( \sum_{i=1}^5 \nabla_{\mathbf{r}_i} \right)^4 + \sum_{i=1}^5 \frac{1}{m_i^3} \nabla_{\mathbf{r}_i}^4 \right), \\ H_{\text{D}} &= -\frac{\pi}{2} \left( \sum_{i=1}^5 \frac{q_0 q_i}{m_i^2} \delta(\mathbf{r}_i) + \sum_{i=1}^5 \sum_{\substack{j=1 \\ j \neq i}}^5 \frac{q_i q_j}{m_i^2} \delta(\mathbf{r}_{ij}) \right), \\ H_{\text{OO}} &= -\frac{1}{2} \sum_{i=1}^5 \frac{q_0 q_i}{m_0 m_i} \left( \frac{1}{r_i} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_i} + \frac{1}{r_i^3} \mathbf{r}_i \cdot (\mathbf{r}_i \cdot \nabla_{\mathbf{r}_i}) \nabla_{\mathbf{r}_i} \right) \\ &\quad -\frac{1}{2} \sum_{i=1}^5 \sum_{\substack{j=1 \\ j \neq i}}^5 \frac{q_0 q_i}{m_0 m_i} \left( \frac{1}{r_i} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} + \frac{1}{r_i^3} \mathbf{r}_i \cdot (\mathbf{r}_i \cdot \nabla_{\mathbf{r}_i}) \nabla_{\mathbf{r}_j} \right) \\ &\quad + \frac{1}{2} \sum_{i=1}^5 \sum_{j > i}^5 \frac{q_i q_j}{m_i m_j} \left( \frac{1}{r_{ij}} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} + \frac{1}{r_{ij}^3} \mathbf{r}_{ij} \cdot (\mathbf{r}_{ij} \cdot \nabla_{\mathbf{r}_i}) \nabla_{\mathbf{r}_j} \right), \\ H_{\text{SS}} &= -\frac{8\pi}{3} \sum_{i=1}^5 \sum_{j > i}^5 \frac{q_i q_j}{m_i m_j} (\mathbf{s}_i \cdot \mathbf{s}_j) \delta(\mathbf{r}_{ij}), \end{aligned}$$

where  $\mathbf{s}_i$  are spin operators for individual electrons and  $\delta(\mathbf{r})$  is the Dirac delta-function.

$E_{\text{QED}}^{(3)}$  is the expectation value of the operator [23–25]

$$\begin{aligned} H_{\text{QED}} &= \sum_{i=1}^5 \sum_{j > i}^5 \left[ \left( \frac{164}{15} + \frac{14}{3} \ln \alpha \right) \delta(\mathbf{r}_{ij}) - \frac{7}{6\pi} P(r_{ij}^{-3}) \right] \\ &\quad + \sum_{i=1}^5 \left( \frac{19}{30} - 2 \ln \alpha - \ln k_0 \right) \frac{4q_0}{3} \delta(\mathbf{r}_i). \quad (3) \end{aligned}$$

Here the expectation value of  $P(r_{ij}^{-3})$  is determined as:

$$\langle P(r_{ij}^{-3}) \rangle = \lim_{a \rightarrow 0} \langle r_{ij}^{-3} \Theta(r_{ij} - a) + 4\pi(\gamma + \ln a) \delta(\mathbf{r}_{ij}) \rangle, \quad (4)$$

where  $\Theta(r)$  and  $\gamma = 0.577\dots$  are the Heaviside step function and the Euler–Mascheroni constant, respectively [23, 24]. In our calculations we did not include the Bethe logarithm,  $\ln k_0$ .

Lastly,  $E_{\text{HQED}}^{(4)}$  is estimated as the expectation value of the following operator

$$H_{\text{HQED}} = \pi q_0^2 \left( \frac{427}{96} - 2 \ln 2 \right) \sum_{i=1}^5 \delta(\mathbf{r}_i), \quad (5)$$

representing the dominant part of the so called one-loop term [15].

The basis functions used in this work to calculate the  $2S$  states of  $^{10}\text{B}$  and  $^{11}\text{B}$  are the following ECG functions:

$$\phi_k = \exp[-\mathbf{r}' (L_k L_k' \otimes I_3) \mathbf{r}], \quad (6)$$

where  $\otimes$  denotes the Kronecker product,  $\mathbf{r}$  is a vector of the internal Cartesian coordinates of the five moving particles (for the B atom  $\mathbf{r}$  is a  $15 \times 1$  vector),  $L_k$  is lower

triangular matrix of nonlinear variation parameters ( $5 \times 5$  matrix), and  $I_3$  is the  $3 \times 3$  identity matrix. Representing the non-linear exponential parameters in the Cholesky-factored form,  $L_k L_k'$ , ensures square integrability of the Gaussian.

The spin-free formalism is used to implement the correct permutational symmetry and properly evaluate all necessary matrix elements. In this formalism, an appropriate symmetry projector is applied to the spatial parts of the wave function to impose the desired symmetry properties. The symmetry projector can be constructed using the standard procedure involving Young operators as described, for example, in ref. [26]. In the case of the  $^2S$  states of boron the permutation operator can be chosen as  $(1 - P_{13})(1 - P_{15} - P_{35})(1 - P_{24})(1 + P_{12})(1 + P_{34})$ , where  $P_{ij}$  denotes the permutation of the spatial coordinates of the  $i$ -th and  $j$ -th electrons. The above operator yields  $5! = 120$  terms for the matrix elements of the Hamiltonian and overlap.

The linear coefficients,  $c_k$ , in the expansion of the wave function in terms of the basis functions and the nonlinear parameters (i.e. matrices  $L_k$ ) are determined by performing a minimization of the total energy based on a multistep approach that employs the analytic gradient [12]. The variational calculations are performed separately and independently for each state, i.e. for each state a different basis set is generated.

The calculations involving growing the basis sets up to 15000 functions are performed for the  $^{11}\text{B}$  boron isotope. Once the basis sets are generated, they are used to perform calculations for the  $^{10}\text{B}$  isotope, as well as for the boron atom with infinite nuclear mass,  $^\infty\text{B}$ . The  $^\infty\text{B}$  results provide a benchmark set of energies for comparison with the conventional BO calculations.

The results of the calculations are summarized in Table I. The table shows the convergence of the nonrelativistic energies of the four  $^2S$  states of  $^{11}\text{B}$  with the number of basis functions. Also the convergence of the expectation values of some operators that contribute to the relativistic and QED corrections are shown. In the table we also present the results for  $^{10}\text{B}$  and  $^\infty\text{B}$  obtained with the largest basis set generated for each state as well as the extrapolated values and estimated uncertainties.

The present results for the lowest  $^2S$  state can be compared with the result of Puchalski *et al.* [8] They used 8192 ECGs and obtained the  $^\infty\text{B}$  non-relativistic energy for the lowest  $^2S$  state of -24.471 393 366 hartree. This is marginally lower than our previous 5100-ECGs result of -24.471 393 06 hartree [7], but less converged than our present result of -24.471 393 609 hartree obtained with 14 000 ECGs. To test how well converged this latter result is, the basis set has been further enlarged to 15 000 ECGs and thoroughly optimized. The  $^\infty\text{B}$  non-relativistic energy obtained is -24.471 393 624 hartree. This value is close to the energy obtained by extrapolation to a complete basis set (see Table I) and testi-

fies to the accuracy level achieved in the present calculations. The basis sets of the remaining three states are also grown to 15 000 ECGs.

Examining further the total non-relativistic energies of  $^{11}\text{B}$  shows that the convergence at the level of  $5 \times 10^{-8}$  hartree (or  $2 \times 10^{-9}$  in relative terms) is reached for the lowest state. For the highest  $6s$  state we estimate the convergence at the level of  $10^{-6}$  hartree (or  $3 \times 10^{-8}$  in relative terms). In order to improve convergence of certain expectation values, we use regularization approaches similar to those described in [9, 10]. Expectation values obtained this way are labelled with a tilde.

The total nonrelativistic energies and the energies that include the relativistic and QED corrections are used to calculate the transition energies between the states. The results are shown in Table II and compared to the values derived from the experimental data [27]. As one can see, the transition energies obtained in the present calculations agree with the experimentally derived values within about  $0.2\text{-}0.3 \text{ cm}^{-1}$ .

The contribution from the relativistic corrections varies with the transition. For the lowest  $4s \rightarrow 3s$  transition it is equal to about  $2.5 \text{ cm}^{-1}$  while for the  $6s \rightarrow 3s$  transition it is equal to about  $10 \text{ cm}^{-1}$ . The inclusion of the lowest order QED correction changes the transition energies by about  $0.3\text{-}1.5 \text{ cm}^{-1}$ , respectively.

By far the largest numerical uncertainty (by this we mean the uncertainty due to the use of finite basis sets) in our calculations comes from the nonrelativistic energy. The numerical uncertainty in relativistic and QED corrections is at least an order of magnitude smaller in absolute terms. However, the second major contributor to the discrepancy between our computed transition energies and the experimental data originates from the missing Bethe logarithm and the approximate nature of expression (5) for  $H_{\text{HQED}}$ . The observed difference provides a rough estimate of the neglected effects.

It is well known that the dominant contribution to the Bethe logarithm in small atoms comes from the core electrons. Thus, these values are very close to each other for different bound states of the same atom (see, for example, [28, 29]). Hence, the corresponding change in the transition energies due to the Bethe logarithm is relatively small. According to our estimates based on the behavior of the Bethe logarithm for  $\text{B}^+$  [29], the uncertainty due to the omitted Bethe logarithm term in our present calculations is of the order of  $0.1\text{-}0.2 \text{ cm}^{-1}$ . Estimating the uncertainty due to missing terms in  $H_{\text{HQED}}$  is a more difficult task. The one-loop term (5) should account for 80-90% of the total  $\alpha^4$  correction to the total energy. However, when the transition energies (e.g. differences) are computed, the contribution due to the one-loop term largely cancels out. Therefore, the missing terms might be equally important. We conservatively estimate the corresponding uncertainty at the level of  $0.01\text{-}0.05 \text{ cm}^{-1}$ .

The present calculations allow for determining the

shifts of the transition energies in going from  $^{11}\text{B}$  to  $^{10}\text{B}$ . The shifts are  $-0.089$ ,  $-0.127$ , and  $-0.188\text{ cm}^{-1}$  for the  $4s \rightarrow 3s$ ,  $5s \rightarrow 3s$ , and  $6s \rightarrow 3s$  transitions, respectively. These shifts are close to the experimental values of  $-0.091(94)$ ,  $-0.117(54)$ , and  $-0.13(20)\text{ cm}^{-1}$  though the experimental uncertainties in those values, particularly for the last one, are quite high.

In summary, a new approach for calculating bound states of small atoms has been developed and implemented. It is used to determine the transition energies between the lowest four  $^2S$  excited states of the  $^{11}\text{B}$  and  $^{10}\text{B}$  isotopes of the boron atom. The nonrelativistic energies of the four states of the main  $^{11}\text{B}$  isotope are calculated with the variational method that makes use of extended sets of all-electron ECG functions, and an approach that does not assume the Born–Oppenheimer approximation. In this we differ from other approaches, such as the one employed by Puchalski *et al.* [8], where the BO energies are calculated first and then corrected for the finite mass of the nucleus using the perturbation theory. Even though the non-BO effect on the total energy of boron is very small and can be adequately described using the perturbation theory, their inclusion in the direct variational calculations, as done in the present work, simplifies the approach adding very little to the computational time. In the second step we calculate the leading  $\alpha^2$  relativistic and QED correction for each state. The comparison of the transition energies with the experimental values shows an agreement at the level of  $0.2\text{--}0.3\text{ cm}^{-1}$ . Lastly, the total energies of the  $^{10}\text{B}$  isotope using the basis sets generated for  $^{11}\text{B}$  are calculated. The differences of the corresponding transition energies of the  $^{11}\text{B}$  and  $^{10}\text{B}$  isotopes give the isotopic shifts, which agree with the experimental values within the experimental error bars.

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TABLE I. Nonrelativistic energies and some key expectation values for the lowest four  $^2S$  states of Boron. All values are in atomic units.

State	Isotope	Basis size	$E_{nr}$	$\langle \tilde{H}_{MV} \rangle$	$\langle \tilde{\delta}(\mathbf{r}_i) \rangle$	$\langle \tilde{\delta}(\mathbf{r}_{ij}) \rangle$	$\langle H_{OO} \rangle$	$\langle \mathcal{P}(1/r_{ij}^3) \rangle$
3s	$^{11}\text{B}$	13000	-24.470143701	-700.2213	14.5067753	0.3581634	-1.554457	-2.9432
	$^{11}\text{B}$	14000	-24.470143716	-700.2213	14.5067753	0.3581634	-1.554457	-2.9431
	$^{11}\text{B}$	15000	-24.470143729	-700.2213	14.5067754	0.3581634	-1.554457	-2.9431
	$^{11}\text{B}$	$\infty$	-24.470143767(25)	-700.2212(8)	14.5067753(3)	0.3581634(1)	-1.554457(1)	-2.9399(20)
	$^{10}\text{B}$	15000	-24.470019330	-700.2072	14.5065565	0.3581587	-1.560082	-2.9430
	$^{10}\text{B}$	$\infty$	-24.470019367(25)	-700.2071(8)	14.5065565(3)	0.3581587(1)	-1.560082(1)	-2.9398(20)
	$^{\infty}\text{B}$	15000	-24.471393622	-700.3632	14.5089743	0.3582113	-1.497933	-2.9437
	$^{\infty}\text{B}$	$\infty$	-24.471393659(25)	-700.3631(8)	14.5089742(3)	0.3582113(1)	-1.497933(1)	-2.9405(20)
4s	$^{11}\text{B}$	13000	-24.401943358	-699.5609	14.4957253	0.3576671	-1.551908	-2.9501
	$^{11}\text{B}$	14000	-24.401943402	-699.5609	14.4957252	0.3576671	-1.551907	-2.9499
	$^{11}\text{B}$	15000	-24.401943437	-699.5608	14.4957252	0.3576671	-1.551907	-2.9493
	$^{11}\text{B}$	$\infty$	-24.401943550(70)	-699.5608(10)	14.4957245(10)	0.3576671(1)	-1.551902(8)	-2.9490(10)
	$^{10}\text{B}$	15000	-24.401819440	-699.5466	14.4955060	0.3576623	-1.557525	-2.9493
	$^{10}\text{B}$	$\infty$	-24.401819553(70)	-699.5466(10)	14.4955054(10)	0.3576623(1)	-1.557520(8)	-2.9489(10)
	$^{\infty}\text{B}$	15000	-24.403189280	-699.7028	14.4979275	0.3577151	-1.495452	-2.9499
	$^{\infty}\text{B}$	$\infty$	-24.403189393(70)	-699.7028(10)	14.4979268(10)	0.3577151(1)	-1.495447(8)	-2.9505(10)
5s	$^{11}\text{B}$	13000	-24.378547448	-699.0706	14.4867591	0.3573243	-1.537166	-2.9572
	$^{11}\text{B}$	14000	-24.378547580	-699.0705	14.4867581	0.3573243	-1.537162	-2.9569
	$^{11}\text{B}$	15000	-24.378547683	-699.0704	14.4867572	0.3573243	-1.537160	-2.9566
	$^{11}\text{B}$	$\infty$	-24.378548020(200)	-699.0701(20)	14.4867533(30)	0.3573242(2)	-1.537144(30)	-2.9560(10)
	$^{10}\text{B}$	15000	-24.378423865	-699.0561	14.4865352	0.3573194	-1.542767	-2.9566
	$^{10}\text{B}$	$\infty$	-24.378424202(200)	-699.0558(20)	14.4865313(30)	0.3573193(2)	-1.542752(30)	-2.9559(10)
	$^{\infty}\text{B}$	15000	-24.379791736	-699.2139	14.4889879	0.3573733	-1.480817	-2.9573
	$^{\infty}\text{B}$	$\infty$	-24.379792072(200)	-699.2136(20)	14.4889837(30)	0.3573732(2)	-1.480800(30)	-2.9566(10)
6s	$^{11}\text{B}$	13000	-24.367924540	-697.3399	14.4539512	0.3561553	-1.464945	-2.9334
	$^{11}\text{B}$	14000	-24.367924960	-697.3395	14.4539458	0.3561551	-1.464929	-2.9331
	$^{11}\text{B}$	15000	-24.367925311	-697.3392	14.4539414	0.3561550	-1.464918	-2.9321
	$^{11}\text{B}$	$\infty$	-24.367926361(700)	-697.3380(80)	14.4539246(200)	0.3561545(6)	-1.464818(80)	-2.9256(50)
	$^{10}\text{B}$	15000	-24.367801782	-697.3237	14.4536955	0.3561493	-1.470453	-2.9320
	$^{10}\text{B}$	$\infty$	-24.367802832(700)	-697.3225(80)	14.4536791(200)	0.3561488(6)	-1.470354(80)	-2.9355(50)
	$^{\infty}\text{B}$	15000	-24.369166472	-697.4951	14.4564106	0.3562124	-1.409293	-2.9330
	$^{\infty}\text{B}$	$\infty$	-24.369167521(700)	-697.4937(80)	14.4563902(200)	0.3562118(6)	-1.409185(80)	-2.9364(50)

TABLE II. Computed  $ns \rightarrow 3s$  transition frequencies (in  $\text{cm}^{-1}$ ) for boron atom in comparison with the values derived from experiment. The subscript (nr, nr + rel, nr + rel + QED, or nr + rel + QED + HQED) indicates the inclusion of relativistic and QED corrections in the calculations.

Transition	Isotope	Basis size	$\Delta E_{\text{nr}}$	$\Delta E_{\text{nr+rel}}$	$\Delta E_{\text{nr+rel+QED}}$	$\Delta E_{\text{nr+rel+QED+HQED}}$
$4s \rightarrow 3s$	$^{11}\text{B}$	13000	14968.245	14970.740	14970.418	14970.410
	$^{11}\text{B}$	14000	14968.239	14970.734	14970.412	14970.404
	$^{11}\text{B}$	15000	14968.234	14970.730	14970.408	14970.400
	$^{11}\text{B}$	$\infty$	14968.217(10)	14970.713(10)	14970.391(10)	14970.383(10)
	$^{11}\text{B}$	Exp. [27]				14970.561(27)
	$^{10}\text{B}$	15000	14968.146	14970.641	14970.320	14970.311
	$^{10}\text{B}$	$\infty$	14968.129(10)	14970.624(10)	14970.302(10)	14970.294(10)
	$^{10}\text{B}$	Exp. [27]				14970.47(9)
$5s \rightarrow 3s$	$^{11}\text{B}$	13000	20103.054	20107.210	20106.627	20106.612
	$^{11}\text{B}$	14000	20103.028	20107.185	20106.602	20106.587
	$^{11}\text{B}$	15000	20103.008	20107.166	20106.583	20106.568
	$^{11}\text{B}$	$\infty$	20102.943(40)	20107.102(40)	20106.518(40)	20106.503(40)
	$^{11}\text{B}$	Exp. [27]				20106.747(20)
	$^{10}\text{B}$	15000	20102.881	20107.039	20106.456	20106.441
	$^{10}\text{B}$	$\infty$	20102.815(40)	20106.975(40)	20106.391(40)	20106.376(40)
	$^{10}\text{B}$	Exp. [27]				20106.63(5)
$6s \rightarrow 3s$	$^{11}\text{B}$	13000	22434.513	22444.254	22442.699	22442.659
	$^{11}\text{B}$	14000	22434.424	22444.166	22442.611	22442.571
	$^{11}\text{B}$	15000	22434.350	22444.094	22442.538	22442.499
	$^{11}\text{B}$	$\infty$	22434.127(150)	22443.874(150)	22442.318(150)	22442.278(150)
	$^{11}\text{B}$	Exp. [27]				22442.50(14)
	$^{10}\text{B}$	15000	22434.159	22443.908	22442.351	22442.311
	$^{10}\text{B}$	$\infty$	22433.936(150)	22443.688(150)	22442.131(150)	22442.091(150)
	$^{10}\text{B}$	Exp. [27]				22442.37(14)

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