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)] nonrelativistic variational calculations performed with all-particle explicitly correlated Gaussian functions and includes the leading relativistic and quantum electrodynamics 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 0.2–0.3 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 opened up ways for numerous applications. However, many of these methods are capable of reaching only 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, quantum electrodynamics (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 $3^1S \to 2^1S$ 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; high precision state-of-the-art fully correlated 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, Komasa, and Pachucki [8] also calculated 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-Born-Oppenheimer (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

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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}B and ^{11}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 $H_{\rm nr}$ for the boron atom has the following form in atomic units (a.u.):

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

where $q_0 = +5$ is the nuclear charge, $q_i = -1$, $i = 1, \ldots, 5$, are charges of the electrons, m_0 is the mass of the nucleus (we used $m_0 = 18\,247.468\,79$ a.u. for ^{10}B and $m_0 = 20\,063.737\,29$ a.u. for ^{11}B), $m_i = 1$, $i = 1, \ldots, 5$, are the electron masses, and $\mu_i = m_0 m_i/(m_0 + m_i)$, $i = 1, \ldots, 5$, 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 μ_i describe the effect of a finite nuclear mass in a nonperturbative 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]:

$$E_{\rm tot} = E_{\rm nr} + \alpha^2 E^{(2)}_{\rm rel} + \alpha^3 E^{(3)}_{\rm QED} + \alpha^4 E^{(4)}_{\rm HQED} \cdots,$$

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

Quantities $E^{(2)}_{\rm rel}$, $E^{(3)}_{\rm QED}$, and others can be evaluated in the framework of the perturbation theory using the non-BO nonrelativistic wave function corresponding to $E_{\rm nr}$ as the zero-order solution. They represent the expectation values of some effective Hamiltonians. In this work, $E^{(2)}_{\rm rel}$ 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:

$$H^{(2)}_{\rm rel} = H_{\rm MV} + H_D + H_{\rm OO} + H_{\rm SS}, \tag{2}$$

traditionally referred to as the mass-velocity, Darwin, orbit-orbit, and spin-spin terms. In the internal coordinates their explicit form is given by [12]

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

$$H_D = -\frac{\pi}{2}\left(\sum_{i=1}^{5}\frac{q_0 q_i}{m_i^2}\delta(\mathbf{r}_i) + \sum_{i=1}^{5}\sum_{\substack{j=1\\ j\neq i}}^{5}\frac{q_i q_j}{m_i^2}\delta(\mathbf{r}_{ij})\right),$$

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

$$H_{\rm SS} = -\frac{8\pi}{3}\sum_{i=1}^{5}\sum_{j>i}^{5}\frac{q_i q_j}{m_i m_j}(\mathbf{s}_i\cdot\mathbf{s}_j)\delta(\mathbf{r}_{ij}),$$

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

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

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

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

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

where $\Theta(r)$ and $\gamma = 0.577\ldots$ 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, $E^{(4)}_{\rm HQED}$ is estimated as the expectation value of the following operator:

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

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}B and ^{11}B are the following ECG functions:

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

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 15×1 vector), L_k is a lower triangular matrix of nonlinear variation parameters (5×5 matrix), and

I_3 is the 3×3 identity matrix. Representing the nonlinear 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 ith and jth 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 15 000 functions are performed for the ^{11}B boron isotope. Once the basis sets are generated, they are used to perform calculations for the ^{10}B isotope, as well as for the boron atom with infinite nuclear mass, $^{\infty}$B. The $^{\infty}$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}B with the number of basis functions. Also, the convergences of the expectation values of some operators that contribute to the relativistic and QED corrections are shown. In the table, we also

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}	$\langle \tilde{H}_{\mathrm{MV}} \rangle$	$\langle \tilde{\delta}(\mathbf{r}_i) \rangle$	$\langle \tilde{\delta}(\mathbf{r}_{ij}) \rangle$	$\langle H_{\mathrm{OO}} \rangle$	$\langle \mathcal{P}(1/r_{ij}^3) \rangle$
3s	^{11}B	13 000	−24.470 143 701	−700.2213	14.506 775 3	0.358 163 4	−1.554 457	−2.9432
	^{11}B	14 000	−24.470 143 716	−700.2213	14.506 775 3	0.358 163 4	−1.554 457	−2.9431
	^{11}B	15 000	−24.470 143 729	−700.2213	14.506 775 4	0.358 163 4	−1.554 457	−2.9431
	^{11}B	∞	−24.470 143 767(25)	−700.2212(8)	14.506 775 3(3)	0.358 163 4(1)	−1.554 457(1)	−2.9399(20)
	^{10}B	15 000	−24.470 019 330	−700.2072	14.506 556 5	0.358 158 7	−1.560 082	−2.9430
	^{10}B	∞	−24.470 019 367(25)	−700.2071(8)	14.506 556 5(3)	0.358 158 7(1)	−1.560 082(1)	−2.9398(20)
	$^{\infty}$B	15 000	−24.471 393 622	−700.3632	14.508 974 3	0.358 211 3	−1.497 933	−2.9437
	$^{\infty}$B	∞	−24.471 393 659(25)	−700.3631(8)	14.508 974 2(3)	0.358 211 3(1)	−1.497 933(1)	−2.9405(20)
4s	^{11}B	13 000	−24.401 943 358	−699.5609	14.495 725 3	0.357 667 1	−1.551 908	−2.9501
	^{11}B	14 000	−24.401 943 402	−699.5609	14.495 725 2	0.357 667 1	−1.551 907	−2.9499
	^{11}B	15 000	−24.401 943 437	−699.5608	14.495 725 2	0.357 667 1	−1.551 907	−2.9493
	^{11}B	∞	−24.401 943 550(70)	−699.5608(10)	14.495 724 5(10)	0.357 667 1(1)	−1.551 902(8)	−2.9490(10)
	^{10}B	15 000	−24.401 819 440	−699.5466	14.495 506 0	0.357 662 3	−1.557 525	−2.9493
	^{10}B	∞	−24.401 819 553(70)	−699.5466(10)	14.495 505 4(10)	0.357 662 3(1)	−1.557 520(8)	−2.9489(10)
	$^{\infty}$B	15 000	−24.403 189 280	−699.7028	14.497 927 5	0.357 715 1	−1.495 452	−2.9499
	$^{\infty}$B	∞	−24.403 189 393(70)	−699.7028(10)	14.497 926 8(10)	0.357 715 1(1)	−1.495 447(8)	−2.9505(10)
5s	^{11}B	13 000	−24.378 547 448	−699.0706	14.486 759 1	0.357 324 3	−1.537 166	−2.9572
	^{11}B	14 000	−24.378 547 580	−699.0705	14.486 758 1	0.357 324 3	−1.537 162	−2.9569
	^{11}B	15 000	−24.378 547 683	−699.0704	14.486 757 2	0.357 324 3	−1.537 160	−2.9566
	^{11}B	∞	−24.378 548 020(200)	−699.0701(20)	14.486 753 3(30)	0.357 324 2(2)	−1.537 144(30)	−2.9560(10)
	^{10}B	15 000	−24.378 423 865	−699.0561	14.486 535 2	0.357 319 4	−1.542 767	−2.9566
	^{10}B	∞	−24.378 424 202(200)	−699.0558(20)	14.486 531 3(30)	0.357 319 3(2)	−1.542 752(30)	−2.9559(10)
	$^{\infty}$B	15 000	−24.379 791 736	−699.2139	14.488 987 9	0.357 373 3	−1.480 817	−2.9573
	$^{\infty}$B	∞	−24.379 792 072(200)	−699.2136(20)	14.488 983 7(30)	0.357 373 2(2)	−1.480 800(30)	−2.9566(10)
6s	^{11}B	13 000	−24.367 924 540	−697.3399	14.453 951 2	0.356 155 3	−1.464 945	−2.9334
	^{11}B	14 000	−24.367 924 960	−697.3395	14.453 945 8	0.356 155 1	−1.464 929	−2.9331
	^{11}B	15 000	−24.367 925 311	−697.3392	14.453 941 4	0.356 155 0	−1.464 918	−2.9321
	^{11}B	∞	−24.367 926 361(700)	−697.3380(80)	14.453 924 6(200)	0.356 154 5(6)	−1.464 818(80)	−2.9256(50)
	^{10}B	15 000	−24.367 801 782	−697.3237	14.453 695 5	0.356 149 3	−1.470 453	−2.9320
	^{10}B	∞	−24.367 802 832(700)	−697.3225(80)	14.453 679 1(200)	0.356 148 8(6)	−1.470 354(80)	−2.9355(50)
	$^{\infty}$B	15 000	−24.369 166 472	−697.4951	14.456 410 6	0.356 212 4	−1.409 293	−2.9330
	$^{\infty}$B	∞	−24.369 167 521(700)	−697.4937(80)	14.456 390 2(200)	0.356 211 8(6)	−1.409 185(80)	−2.9364(50)

present the results for ^{10}B and $^{\infty}$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, Komasa, and Pachucki [8]. They used 8192 ECGs and obtained the $^{\infty}$B nonrelativistic 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 $^{\infty}$B nonrelativistic energy obtained is −24.471393622 hartree. This value is close to the energy obtained by extrapolation to a complete basis set (see Table I) and testifies 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 nonrelativistic energies of ^{11}B shows that the convergence at the level of 5×10^{-8} hartree (or 2×10^{-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 3×10^{-8} in relative terms). In order to improve the convergence of certain expectation values, we use regularization approaches similar to those described in Refs. [9,10]. Expectation values obtained this way are labeled 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 0.2–0.3 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 cm^{-1}, while for the $6s \rightarrow 3s$ transition it is equal to about 10 cm^{-1}. The inclusion of the lowest-order QED correction changes the transition energies by about $0.3 - 1.5$ 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_{HQED}.

TABLE II. Computed $ns \rightarrow 3s$ transition frequencies (in cm^{-1}) for the boron atom in comparison with the values derived from the 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	ΔE_{nr}	$\Delta E_{\mathrm{nr+rel}}$	$\Delta E_{\mathrm{nr+rel+QED}}$	$\Delta E_{\mathrm{nr+rel+QED+HQED}}$
$4s \rightarrow 3s$	^{11}B	13 000	14 968.245	14 970.740	14 970.418	14 970.410
	^{11}B	14 000	14 968.239	14 970.734	14 970.412	14 970.404
	^{11}B	15 000	14 968.234	14 970.730	14 970.408	14 970.400
	^{11}B	∞	14 968.217(10)	14 970.713(10)	14 970.391(10)	14 970.383(10)
	^{11}B	Exp. [27]				14 970.561(27)
	^{10}B	15 000	14 968.146	14 970.641	14 970.320	14 970.311
	^{10}B	∞	14 968.129(10)	14 970.624(10)	14 970.302(10)	14 970.294(10)
	^{10}B	Exp. [27]				14 970.47(9)
$5s \rightarrow 3s$	^{11}B	13 000	20 103.054	20 107.210	20 106.627	20 106.612
	^{11}B	14 000	20 103.028	20 107.185	20 106.602	20 106.587
	^{11}B	15 000	20 103.008	20 107.166	20 106.583	20 106.568
	^{11}B	∞	20 102.943(40)	20 107.102(40)	20 106.518(40)	20 106.503(40)
	^{11}B	Exp. [27]				20 106.747(20)
	^{10}B	15 000	20 102.881	20 107.039	20 106.456	20 106.441
	^{10}B	∞	20 102.815(40)	20 106.975(40)	20 106.391(40)	20 106.376(40)
	^{10}B	Exp. [27]				20 106.63(5)
$6s \rightarrow 3s$	^{11}B	13 000	22 434.513	22 444.254	22 442.699	22 442.659
	^{11}B	14 000	22 434.424	22 444.166	22 442.611	22 442.571
	^{11}B	15 000	22 434.350	22 444.094	22 442.538	22 442.499
	^{11}B	∞	22 434.127(150)	22 443.874(150)	22 442.318(150)	22 442.278(150)
	^{11}B	Exp. [27]				22 442.50(14)
	^{10}B	15 000	22 434.159	22 443.908	22 442.351	22 442.311
	^{10}B	∞	22 433.936(150)	22 443.688(150)	22 442.131(150)	22 442.091(150)
	^{10}B	Exp. [27]				22 442.37(14)

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 B^+ [29], the uncertainty due to the omitted Bethe logarithm term in our present calculations is of the order of 0.1–0.2 cm^{-1}. Estimating the uncertainty due to missing terms in H_{HQED} is a more difficult task. The one-loop term (5) should account for 80%–90% of the total α^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 0.01–0.05 cm^{-1}.

The present calculations allow for determining the shifts of the transition energies in going from ^{11}B to ^{10}B. The shifts are -0.089, -0.127, and $-0.188\ \mathrm{cm}^{-1}$ for the $4s \to 3s$, $5s \to 3s$, and $6s \to 3s$ transitions, respectively. These shifts are close to the experimental values of $-0.091(94)$, $-0.117(54)$, and $-0.13(20)\ \mathrm{cm}^{-1}$, 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}B and ^{10}B isotopes of the boron atom. The nonrelativistic energies of the four states of the main ^{11}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, Komasa, and Pachucki [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 α^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 0.2–0.3 cm^{-1}. Lastly, the total energies of the ^{10}B isotope using the basis sets generated for ^{11}B are calculated. The differences of the corresponding transition energies of the ^{11}B and ^{11}B isotopes give the isotopic shifts, which agree with the experimental values within the experimental error bars.

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