Explicitly correlated wave function for a boron atom

Mariusz Puchalski,1 Jacek Komasa,1 and Krzysztof Pachucki2
1Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznań, Poland
2Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warsaw, Poland
(Dated: November 24, 2015)

We present results of high-precision calculations for a boron atom’s properties using wave functions expanded in the explicitly correlated Gaussian basis. We demonstrate that the well-optimized 8192 basis functions enable a determination of energy levels, ionization potential, and fine and hyperfine splittings in atomic transitions with nearly parts per million precision. The results open a window to a spectroscopic determination of nuclear properties of boron including the charge radius of the proton halo in the 8B nucleus.

PACS numbers: 31.15.ac, 31.30.J-

INTRODUCTION

While for hydrogenic ions the nonrelativistic wave function is known exactly, for all larger atomic systems it has to be obtained numerically, most often with the help of the variational principle. The numerical precision achieved for a few electron systems can, nevertheless, be very high. For example, nonrelativistic energies of the He atom are known with more than 20 digits of accuracy [1–3], of Li with 15 digits [4, 5], and very recently the precision achieved for the Be atom reached 11 significant digits [6–8]. The computational approach employed in all those atomic studies is based on explicitly correlated functions of the exponential or Gaussian form, which are the best known representations of the nonrelativistic wave function. For three-electron systems, the most accurate solution of the Schrödinger equation is obtained with the Hylleraas (exponential times polynomial) basis functions [4, 5, 9]. In such systems, the accuracy of the theoretical predictions for transition energies and isotope shifts is limited by the approximate treatment of higher-order ∼ mα6,7 QED corrections rather than by numerical inaccuracies of the nonrelativistic wave function. Methods with Hylleraas functions have been extended to four-electron atomic systems but only for some restricted selection of basis functions, because of significant difficulties in evaluation of matrix elements [10, 11]. Even more difficult integrals appear in the matrix elements of relativistic operators. Unquestionably, significant efforts have to be made to improve the Hylleraas approach, in order for it to be practical for the four and more electron systems. Therefore, at present, the method of choice for such systems is that based on explicitly correlated Gaussian (ECG) functions. The effectiveness of the ECG functions in treating few-electron problems has already been demonstrated by high-precision calculations of the nonrelativistic energies of atomic and molecular systems [12–17]. In particular, for the beryllium atom the highest accuracy has been obtained using the ECG functions [7, 18–21]. The main advantage of the ECG method is that the underlying integration is manageable and very fast in numerical evaluation due to the compact formulas involving only elementary functions. On the other hand, the Gaussian functions have the drawback of improper asymptotic behavior since they decay too fast at long interparticle distances. They also have an incorrect short-range form and fail to correctly describe the Kato cusp. However, these two flaws can be overcome if one employs a sufficiently large and well-optimized ECG basis set. The issue is subtler in calculations of relativistic and QED properties, in which the local inaccuracies of the wave functions result in significant numerical loss of mean values. One has to carefully optimize over a large number (oftentimes exceeding 105) of variational parameters matching local behavior of the exact wave function and employ dedicated techniques which accelerate the convergence of nearly singular matrix elements [22]. An additional drawback of the approach based on fully correlated functions is the cost resulting from antisymmetrization of the wave function which grows like N! with the number of electrons N.

In this paper we demonstrate that in spite of this high evaluation costs, the methods based on ECG functions may give a spectroscopic accuracy for five-electron systems, such as the boron atom, in a realistic computational time. We report on the calculation of nonrelativistic energies of the ground 2P and the excited 3S levels, and the leading relativistic corrections including the fine and hyperfine structure of the ground state. The achieved numerical accuracy is several orders higher than those of any previous calculations and not always in agreement with them. In addition, we provide accurate results for a four-electron B+ ion needed to determine the ionization potential of the boron ground state.

NONRELATIVISTIC HAMILTONIAN AND CORRECTIONS

The determination of accurate wave functions corresponding to the nonrelativistic, clamped nucleus Hamiltonian (in natural units)

\[ H_0 = \sum_a \frac{p_a^2}{2m} - \sum_a \frac{Z \alpha}{r_a} + \sum_{a>b} \frac{\alpha}{r_{ab}}. \]  

(1)

is the main subject of this paper. If the wave function \( \Phi \) is determined, all the corrections to the energy \( E_0 \) in the following perturbative expansion in the fine-structure constant...
\[ \alpha \sim 1/137 \]

\[ E = E^{(2)} + E^{(4)} + E^{(5)} + E^{(6)} + \ldots, \quad E^{(n)} \sim \frac{m\alpha^n}{n!} \quad (2) \]

can be expressed in terms of expectation values \( \langle \Phi | \ldots | \Phi \rangle \equiv \langle \ldots \rangle \) of known operators. Complete nonrelativistic energy \( E^{(2)} \) consists of the clamped nucleus energy \( E_0 \) and the kinetic energy of the nucleus \( H_N \), which can be calculated in the center of mass frame as a small perturbation,

\[ H_N = \frac{\mu_N^2}{2m_N} = m_N \left( \sum_a \frac{p_a^2}{2m_N} + \sum_{a<b} \frac{\vec{p}_a \cdot \vec{p}_b}{m_N} \right), \quad (3) \]

where \( m_N \) is the nuclear mass. The leading relativistic \( E^{(4)} \) correction is calculated as the mean value of the Breit-Pauli Hamiltonian given by

\[ H^{(4)} = H_{as} + H_{fs} + H_{hfs}, \quad (4) \]

\[ H_{as} \equiv \sum_a \left[ -\frac{p_a^4}{8m^3} + \frac{Z\alpha}{2m^2} \delta^3(\vec{r}_a) \right] \quad (5) \]

\[ + \sum_{a>b} \left[ \frac{Z\alpha}{4m^2} \delta^3(\vec{r}_{ab}) - \frac{\alpha}{2m^2} \left( \frac{\delta^3(\vec{r}_{ab})}{r_{ab}} + \frac{r_{ab}^3}{r_{ab}} \right) \right] p_b^2, \]

\[ H_{fs} \equiv \sum_a \frac{Z\alpha}{4m^2} \left[ (g-1) \vec{r}_a \times \vec{p}_a \right] \cdot \vec{\sigma}_a \]

\[ + \sum_{a\neq b} \frac{\alpha g^2}{16m^2} \left( \vec{\sigma}_a \cdot (g \vec{r}_{ab} \times \vec{p}_b - (g-1) \vec{r}_{ab} \times \vec{p}_a) \right) \delta^3(\vec{r}_{ab}) \quad (6) \]

The leading order Hamiltonian for the hyperfine splitting is

\[ H_{hfs} \equiv \sum_a \left[ \frac{1}{3} \frac{Z\alpha g}{m_N} \delta^3(\vec{r}_a) \right] \left( \vec{\sigma}_a \cdot \vec{I} \right) \quad (7) \]

where \( I \) is the nuclear spin, \( g \) is the electron g factor, \( Q_N \) is the electric quadrupole moment of the nucleus, and \( g_N \) is the nuclear g factor

\[ g_N = \frac{m_N}{Zm_p} \mu \frac{1}{I} \quad (8) \]

It is convenient to rewrite the expectation value of the hyperfine splitting \( H_{hfs} \), Hamiltonian in terms of commonly used \( A_J \) and \( B_J \) coefficients,

\[ \langle H_{hfs} \rangle_J = A_J \vec{I} \cdot \vec{J} + \frac{B_J}{6} \frac{3(I^3 J^3)(2) 3(J^3 J^3)(2)}{(2I-1)(2J-1)}, \quad (9) \]

where \( J \) is the total electronic angular momentum. For this purpose we decompose \( H_{hfs} \)

\[ H_{hfs} = \vec{I} \cdot \vec{G} + \frac{G^{ij}}{6} \frac{3(I^3 J^3)(2) 3(J^3 J^3)(2)}{(2I-1)(2J-1)} \quad (10) \]

and these coefficients are

\[ A_J = \frac{1}{J(J+1)} \langle \vec{J} \cdot \vec{G} \rangle, \quad (11) \]

\[ B_J = \frac{2}{(2J+3)(J+1)} \langle J^3 J^3 G^{ij} \rangle. \quad (12) \]

Higher-order corrections to the atomic energy originate from QED. They are significantly smaller than \( E^{(4)} \) because of the higher powers of \( \alpha \):\n
\[ E^{(5)} = \frac{4Z^2 \alpha^2}{3m^2} \left[ \frac{19}{30} + \ln(\alpha^2) - \ln k_0 \right] \sum_a \langle \delta^3(\vec{r}_a) \rangle \quad (13) \]

\[ + \frac{\alpha^2}{m^2} \left[ \frac{164}{15} + 14 \ln 3 \right] \sum_{a<b} \langle \delta^3(\vec{r}_{ab}) \rangle, \]

\[ E^{(6)} \approx \frac{7Z^2}{6} \frac{m\alpha^2}{m^2} \left[ \frac{427}{96} - 2\ln(2) \right] \sum_a \langle \delta^3(\vec{r}_a) \rangle. \quad (14) \]

**REDUCTION OF MATRIX ELEMENTS**

We represent the wave function \( \Phi^{i} \) of the five-electron \( ^2P \) atomic state in the form

\[ \Phi^{i} = \sqrt{\frac{1}{5!}} A \left( \sum_n t_n \phi_{n}^{i} \{ \vec{r}_{a} \} \chi_{(a)} \right) \quad (15) \]

where \( t_n \) is a linear coefficient, \( \chi_{(a)} \) is the spin wave function

\[ \chi_{(a)} = (\alpha_1 \beta_2 - \beta_1 \alpha_2) (\alpha_3 \beta_4 - \beta_3 \alpha_4) (\alpha_5) \quad (16) \]

and \( \{ a \} \) and \( \{ \vec{r}_{a} \} \) denote the sequences 1, 2, 3, 4, 5 and \( r_1, r_2, r_3, r_4, r_5 \), respectively. The symbol \( A \) denotes antisymmetrization and \( \phi^{i} \{ \vec{r}_{k} \} \) is a spatial function with Cartesian index \( i \) that comes from one of the electron coordinates

\[ \phi^{i} \{ \vec{r}_{k} \} = r_{m} \exp \left[ -\sum_{k=1}^{N} a_{k} r_{k}^{2} - \sum_{t>k=1}^{N} b_{kl} r_{k}^{2} \right]. \quad (17) \]

The normalization we assume is

\[ \sum_{i} \langle \Phi^{i} | \Phi^{i} \rangle = \sum_{n} \sum_{m} t_{n}^{*} t_{m} \sum_{i} \langle \phi_{n}^{i} | \phi_{m}^{i} \rangle_S = 1 \quad (18) \]

where

\[ \langle \phi^{i} | \phi^{i} \rangle_S = \langle \phi^{i} \{ \vec{r}_{a} \} | P_{\{a\}} e_{\{a\}} \phi^{i} \{ \vec{r}_{a} \} \rangle = 1 \quad (19) \]

and where \( P_{\{a\}} \) denotes the sum over all permutations of \( \{ a \} \).

From now on we will assume that a repeated Cartesian index
is implicitly summed up. We introduce also another type of a matrix element, which will be used later
\[
\langle \phi^i | Q | \phi^k \rangle_F = \sum_c \langle \phi^i | \{ \vec{r}_a \} | Q_c | \phi^k \rangle_F c_c \phi^k(\{ \vec{r}_b \}).
\] (20)

The \( c_c \) coefficients are integers and depend on the permutation \( \{ \alpha \} \). Since the number of permutations is \( 6! = 120 \), we cannot explicitly write them down here. What is important is that all the matrix elements are either of the standard form \( \langle \ldots | S \rangle \) with the constant coefficients \( c_c \) or of the Fermi interaction form \( \langle \ldots | F \rangle \) with the \( c_c \) coefficients.

The \( ^2P_{1/2} \) and \( ^2P_{3/2} \) wave functions are constructed using Clebsch-Gordan coefficients. Expectation values with these wave functions can be reduced to spinless expressions with an algebraic prefactor \( K_J \) for \( J = 1/2 \) and \( 3/2 \). Namely, for an operator \( Q \), the first-order matrix elements with an auxiliary notation \( \{ K_{1/2}, K_{3/2} \} \) take the form
\[
\langle \Phi | Q | \Psi \rangle = \{ 1, 1 \} \langle \phi^i | Q | \phi^k \rangle_S ,
\] (21)
\[
\langle \Phi | \sum_c \tilde{\sigma}_c \cdot \vec{Q}_c | \Psi \rangle = \{ 1, -1/2 \} i \epsilon^{ijk} \langle \phi^i | Q | \phi^k \rangle_F ,
\] (22)
\[
\frac{1}{J(J+1)} \langle \Phi | J^i \cdot \sum_c \tilde{\sigma}_c Q_c | \Psi \rangle = \{ -2/3, 2/3 \} \langle \phi^i | Q | \phi^k \rangle_F ,
\] (23)
\[
\frac{1}{J(J+1)} \langle \Phi | J^i \cdot \vec{Q} | \Psi \rangle = \{ -2/3, -1/3 \} i \epsilon^{ijk} \langle \phi^i | Q | \phi^k \rangle_F S ,
\] (24)

\begin{table}[h]
\begin{tabular}{|c|c|c|c|}
\hline
Basis size & \( 2^2P \) & \( 3^2S \) & \( 2^1S(B^+) \) & Ref. \\
\hline
4096 & -24.653 864 204 & -24.471 391 933 & -24.348 884 458 05 & \ \\
8192 & -24.653 867 537 & -24.471 393 366 & - & \ \\
\infty & -24.653 868 05(45) & -24.471 393 68(32) & -24.348 884 479(14) & \ \\
10000 & - & - & - & \ \\
\hline
\end{tabular}
\end{table}

The above spin reduced matrix elements involve only scalars built of spatial variables \( \vec{r}_a \), and therefore they all can easily be expressed by Gaussian type integrals.

**NUMERICAL CALCULATIONS AND RESULTS**

In the numerical calculations we employed the ECG basis functions of progressively doubled size from 1024 to 8192 terms for the B atom, and from 512 to 4096 terms for the \( B^+ \) ion. The nonlinear parameters were optimized variationally with respect to \( E_0 \) until the energy reached stability in a desired number of digits. The sequence of energies obtained for consecutive basis sets enables estimation of the basis truncation error. The convergence for the \( 2^2P \) and \( 3^2S \) levels of B, and the \( 2^1S \) state of the \( B^+ \) ion is presented in Table I. The variational energies obtained from the largest expansion are lower than the best results previously reported in [23, 24].

In a similar way, i.e. from the convergence with the growing basis set size, the truncation errors of the expectation values of various operators were estimated. Particular care was taken for the singular or nearly singular operators \( \langle p^a, \delta^3(r_a), \delta^3(r_{ab}), P(r_{ab}^-) \rangle \), which exhibit a slow numerical convergence of their mean values. This undesirable effect is particularly pronounced for the ECG functions having improper short-distance behavior. The solution is to employ
TABLE II: Expectation values of various spinless and fine-structure operators for $2^2P$ and $3^2S$ states of boron atom. To obtain the mean values for $2^2P_J$, the value for $2^2P_1$ state has to be multiplied by the relevant $\{K_{1/2}, K_{3/2}\}$ coefficient in curly bracket i.e. \{1, $-\frac{1}{2}$\} following Eqs. (21) – (26).

<table>
<thead>
<tr>
<th>Operator</th>
<th>$2^2P$</th>
<th>$3^2S$</th>
<th>$2^1S(B^+)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_0$</td>
<td>$-24.653\ 868\ 1(5)$</td>
<td>$-24.471\ 393\ 7(3)$</td>
<td>$-24.348\ 884\ 479\ (14)$</td>
</tr>
<tr>
<td>$\vec{p}_a \cdot \vec{p}_b$</td>
<td>$0.271\ 175(2)$</td>
<td>$0.607\ 784(3)$</td>
<td>$0.595\ 137\ 52(4)$</td>
</tr>
<tr>
<td>$p^4_a$</td>
<td>$5.546.924(3)$</td>
<td>$5.602.919(2)$</td>
<td>$5.598.710\ (4)$</td>
</tr>
<tr>
<td>$\delta(r_a)$</td>
<td>$71.864\ 97(3)$</td>
<td>$72.544\ 82(2)$</td>
<td>$72.506\ 327(3)$</td>
</tr>
<tr>
<td>$\delta(r_{ab})$</td>
<td>$3.538\ 453.2(14)$</td>
<td>$3.582\ 111.2(7)$</td>
<td>$3.577\ 866.33(12)$</td>
</tr>
<tr>
<td>$p^4_b (\frac{\delta_b}{r_{ab}} + \frac{\delta_a r_{ab}}{r_{ab}}) p^4_b$</td>
<td>$2.171\ 606(3)$</td>
<td>$2.995\ 875(3)$</td>
<td>$3.025\ 198\ 47(14)$</td>
</tr>
<tr>
<td>$\vec{p}_a \times \vec{p}_b \cdot \vec{\sigma}_a$</td>
<td>$-1.494\ 336(5)$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>$\vec{r}_{ab} \times \vec{p}_a \cdot \vec{\sigma}_a$</td>
<td>$-2.855\ 953(3)$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>$\vec{r}_{ab} \times \vec{p}_b \cdot \vec{\sigma}_a$</td>
<td>$0.568\ 459(4)$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>$P(r_{ab})$</td>
<td>$-27.874\ 22(6)$</td>
<td>$-29.391\ 67(4)$</td>
<td>$-29.459\ 453(0)$</td>
</tr>
<tr>
<td>$\ln k_0$</td>
<td>$6.195(5)^a$</td>
<td>$6.195(5)^a$</td>
<td>$6.194\ 4(9)^b$</td>
</tr>
</tbody>
</table>

$^a$ estimated from $\ln k_0[2^1S(B^+)]$

$^b$ Ref. [23]

CONCLUSIONS

We calculated the energy levels, isotope shifts, and fine and hyperfine structure in the atomic boron with numerical pre-

 تركيبات متعددة (CC) مبني على ترددات إلكترونية واحدة لا يوفرون النتائج ذات الدقة المطلوبة.

النتائج القيمية للتفاعل الالهترائي المجهول مقدمة في الجداول IV و V. السابق الجدول يحتوي على التوقعات القيمية لجدد التفاعلات الفاصلة المجهولة التي تحتوي على الـ $H_{hfs}$ متوسط التفاعل والكيد الاصلي والجهد الكهربائي تكوين. الإشارة من عنوان هذه الجدول تقدم توقعات القيمة التالية لتحياء التفاعلات الفاصلة العادة المستخدمة تعديلات البارامترات المحتمل في استخدامها. نلاحظ أن الفروقات الملمة في التفاعلات الفاصلة الفردية في الجدول IV مع النتائج من الإجراءات السابقة لchen [27]. هذا مخصوصmente بين محل في التفاعل البارامتر $a_e$ الذي يعبر عن الفروقات هذه الفروقات 25%%. صادمًا، الفروقات بين نتائج Chen وفواتي إعداد التفاعلات A-التفاعل الالهترائي دائمًا ما يقارن بال степن من $Z\alpha^2$ اللمكي الالهترائي، لكثير من CARES من $A\sigma^2$ التباين $A$ أو $B$ معامل. النتائج النهائية للمد التكوين $2^2P$ والورقة $1^1B$ و$1^3B$ مترجمة في الجدول V.
All entries in \( \text{cm}^{-1} \) and of the ground level energy for the accurate determination of the isotope shift in the value for the mass polarization correction (see Tab. II) permits of the atomic computational methods. Moreover, the precise insensitivity to the not-well-known nuclear finite size effects, being exceptionally small for the splitting and for the Fermi contact interaction, the last one being exceptionally small for the \( 2P \) ground state. The smallness of the Fermi contact term makes the hyperfine splitting insensitive to the not-well-known nuclear finite size effects, thus the comparison with experimental hfs will be a good test of the atomic computational methods. Moreover, the precise value for the mass polarization correction (see Tab. II) permits the accurate determination of the isotope shift in the \( 2P - 3S \) transition, which paves the way for determination of the nuclear charge radius of the proton halo in the \( ^8\text{B} \) nucleus, as we have already demonstrated for the beryllium atom [8].

### Acknowledgments

This research was supported by National Science Center (Poland) Grant No. 2014/15/B/ST4/05022 as well as by a computing grant from Poznań Supercomputing and Network-
ing Center and by PL-Grid Infrastructure.