

Doublet-quartet energy separation in boron: A partitioned-correlation-function-interaction method

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No lines have been observed for transitions between the doublet and quartet levels of B I. Consequently, energy levels based on observation for the latter are obtained through extrapolation of wavelengths along the isoelectronic sequence for the $2s^2 2p^2 P_{3/2}^o - 2s 2p^2 P_{5/2}^o$ transition. In this paper, accurate theoretical excitation energies from a partitioned-correlation-function-interaction (PCFI) method are reported for B I that include both relativistic effects in the Breit-Pauli approximation and a finite mass correction. Results are compared with extrapolated values from observed data. For B I our estimate of the excitation energy $28\,959 \pm 5 \text{ cm}^{-1}$ is in better agreement with the values obtained by Edlén *et al.* (1969) than those reported by Kramida and Ryabtsev (2007). Our method is validated by applying the same procedure to the separation of these levels in C II.

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I. INTRODUCTION

Intercombination lines are not observed in B I, hence the position of the quartets relative to the doublets is obtained by the extrapolation of wavelengths from observed data for the $2s^2 2p^2 P_{3/2}^o - 2s 2p^2 P_{5/2}^o$ transition along the isoelectronic sequence. Edlén *et al.* [1] relied on nonrelativistic theory to scale available excitation energies by an effective nuclear charge $Z - 2.97$, where Z is the atomic number. The screening parameter of 2.97 was chosen to yield a curve with minimum variation. Edlén *et al.* estimated the energy separation of the levels in B I to be $28\,866 \pm 15 \text{ cm}^{-1}$. Recently, Kramida and Ryabtsev [2] revised the position of the $2s 2p^2 P_{5/2}^o$ level, using an extended set of experimental data over the range $Z = 6$ to 14. Their revised estimate for the energy separation is $28\,643.1 \text{ cm}^{-1}$ with an uncertainty of 1.8 cm^{-1} that does not include the extrapolation error. This revised value is now included in the Atomic Spectra Database (ASD) [3]. The difference in the Edlén *et al.* and Kramida and Ryabtsev values is 223 cm^{-1} .

Multiconfiguration Hartree-Fock calculations with relativistic corrections in the Breit-Pauli (MCHF + BP) approximation have been reported for the boronlike isoelectronic sequence by Tachiev and Froese Fischer [4]. For B I, C II, and N III, the computed 4P levels were too *high* relative to ASD values [3] of that time by (0.53, 0.13, 0.10)%, respectively. With the revision (now adopted in ASD), this error in B I has

increased to 1.3% or 277 cm^{-1} . Such a large error for boron compared with the error for other elements is surprising.

Boron is a relatively light atom in which the fine-structure splitting is small and the spin-orbit interaction between different LS terms is negligible. For this reason, earlier “spectrum” calculations (for energy levels relative to the ground state rather than total energies) were often restricted to doublet terms [5]. The MCHF + BP calculation by Tachiev and Froese Fischer was intended as a spectrum calculation for all levels of the lower portion of the spectrum for the isoelectronic sequence, with the neutral atom not the element of prime concern. In particular, correlation in the $1s^2$ core was omitted since its contribution to the wave function in the outer region of the atom decreases rapidly along the isoelectronic sequence. With current computers and techniques for treating correlation, calculations of considerably higher accuracy are feasible.

For light atoms, Hylleraas-CI methods are often the most accurate, and considerable progress has been made for the $^2P^o$ ground state energy [6] of boron, but it is not yet the most accurate. Using state of the art configuration interaction methods with energy optimized Slater-type orbitals, Almora-Díaz and Bunge [7] obtained a nonrelativistic ground state energy of $-24.653\,861(2)E_h$ (Hartree units), with an uncertainty of less than 0.5 cm^{-1} . Recently results from correlated-Gaussian [8] calculations have been reported with a slightly lower energy of $-24.653\,866\,08(250)E_h$ for a nucleus of infinite mass, an energy that increased when the finite mass effect was included. The latter, very detailed calculation, is in a class of its own, requiring one year of continuous computing on a

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multiprocessor system employing 16 to 24 cores. In neither of these papers were results available for the $4P$ excited state and relativistic effects were not considered. The “exact” nonrelativistic total energy has been derived from observed data to be $-24.65393E_h$ [9].

Relativistic energies relative to the ground state have been reported by Safronova *et al.* [10] obtained by applying perturbation theory to the calculation of energies for various values of Z . For boron, the energy of $2s2p^2\ ^4P_{5/2}$ relative to $2s^22p\ ^2P_{3/2}^o$ was $29\,688\text{ cm}^{-1}$, considerably higher than the Kramida and Ryabtsev value. This excitation energy can be calculated from Gu’s total energies [11] as an even higher value of $29\,917.06\text{ cm}^{-1}$ from a fully relativistic, combined configuration interaction and many-body perturbation theory method, but does not claim high accuracy.

In this paper we report the results of calculations for the $2s^22p\ ^2P_{3/2}^o - 2s2p^2\ ^4P_{5/2}$ excitation energy, both in the MCHF+BP method tailored to the neutral atom, and results from a partitioned-correlation-function-interaction (PCFI) method that allows nonorthogonal orbital bases for the inclusion of different correlation effects [12,13]. Relativistic and finite mass corrections are included. Accuracy is estimated and validated by similar calculations for C II where experimental data are available.

II. THE MCHF METHOD: THEORY AND RESULTS

In the multiconfiguration Hartree-Fock method [14], the wave function $\Psi(\gamma LS)$ for the state labeled γLS is a linear combination of configuration state functions (CSFs) defined in terms of an orthonormal orbital basis. The ATSP2K code [15] can be used to determine the optimal basis and CSF expansion coefficients that define a stationary energy. In the present case, since both states are lowest in their symmetry, the optimal solution minimizes the total energy of the state. The accuracy of the computed energy relative to the exact energy of the state depends largely on the CSFs included in the expansion and the orbital basis.

In this work, systematic calculations were performed in which the orbital basis was increased from one calculation to the next by increasing the maximum principal quantum number n , thereby introducing a new “layer” of orbitals. This parameter n characterizes the calculation. MCHF calculations up to $n = 9$ were performed with orbital quantum numbers up to $l = 5$ (h orbitals).

The computational model determines the CSF space for each orbital set. The LSGEN program [16] was used to generate all CSFs that differ by one or more electrons from a given configuration and are of the same parity and LS quantum numbers. Such substitutions are referred to as single (S), double (D), etc. excitations. For open-shell systems, SD excitations from a single configuration are not sufficient, as shown for the Be ground state [12,14]. On the other hand, a complete active space (CAS) expansion for which the number of excitations equals the number of electrons, soon becomes impractical as the orbital set increases. Here we have used a method, referred to as MR-SD, that starts with a multireference set (MR) of CSFs that includes the CSF for the state and any others that may be important. Then SD expansions are obtained by applying the process to each member of the MR set.

Ideally, the MR set should contain all the important CSFs of the final wave function. An indication of these CSFs can be obtained from a small MCHF calculation, such as an MCHF calculation for an $n = 3$ SD expansion. Those with small expansion coefficients can be omitted, but as more correlation is added, others may gain importance. In the present work, the default MR sets are

$$\begin{aligned} {}^2P^o &: 2s^22p, 2p^3, 2s2p3d, 2s^23p, 2s3s3p, 2p^23p, 2p3s^2, \\ &2p3d^2, 2s2p3s, \\ {}^4P &: 2s2p^2, 2s2p3p, 2p^23d, 2s3d^2, 2s3p^2, 2p3s3p, 2p^23s. \end{aligned} \quad (1)$$

In the final wave function, the smallest expansion coefficient was about 0.025 in magnitude, accounting for $\approx 0.06\%$ of the eigenvector composition.

The present two states of interest have a common $1s^2$ core and three valence electrons. The substitution of one or two valence orbitals by other orbitals defines valence-valence (VV) correlation, substitution of a single $1s$ orbital, and possibly also one valence orbital defines core-valence (CV) correlation, and substitution of the two $1s$ orbitals defines core-core (CC) correlation. Correlation in the core essentially cancels in the calculation of an energy difference, but it may be large. Therefore, small differences may contribute significantly to the energy separation. In order to maintain this balance at intermediate stages, prior to convergence, the variational principle was applied to the sum of energy functionals for each state, referred to as simultaneous optimization. Since both states are lowest in their symmetry, the sum of the energies is also a minimum. In this way, the same orbitals were used in the calculation of the core of both states and the optimization process minimized the combined energy.

Table I shows the variation of the ${}^2P^o - {}^4P$ excitation energy for several different computational strategies all using the MCHF method in which all orbitals are optimized unless specified to the contrary.

In the *independent* strategy (used in calculation [A]), the wave function for each state is calculated independently in a single orthonormal orbital basis that then describes all three types of correlation. As shown previously [12], the orbitals for VV correlation will have a maximum in the outer region of the atom, the CV orbitals are in the regions of overlap between $1s$ and $2s$ or $2p$, and CC is in the region of the $1s$ orbital. At each stage of a systematic calculation, the orbitals arrange themselves so as to minimize the energy and, in going from one layer to the next, considerable rearrangements may occur. If the rearrangements of the orbitals in the two independent calculations are not similar at an intermediate stage, an imbalance *may* occur in the difference.

In the *simultaneous* strategy (used in calculation [B]), the variational procedure is applied to the sum of the two energies so that the same orbitals are used to describe both wave functions. In particular, the more dynamic CC correlation is described in terms of the same orbitals. Table I shows that, with the same MR-SD expansion, the simultaneous optimization method closely tracks calculation [A], although the excitation energy is somewhat larger. No large differences were found, even though the total energy of the 4P was raised more than that of ${}^2P^o$, thereby increasing ΔE , but the difference decreased

TABLE I. Comparison of the $2s^2 2p^2 P^o - 2s 2p^2 {}^4P$ excitation energy, ΔE in cm^{-1} , for various computational strategies (see text for details). The number of CSFs, N , and the total energies, E in E_h , corresponding to the largest active set ($9h$) wave functions for the ${}^2P^o$ and 4P terms are given at the end of the table.

n	ΔE ([A])	ΔE ([B])	ΔE ([C])	ΔE ([D])	ΔE ([E])
4	28 301.91	28 318.01	28 319.91	28 382.21	28 677.73
5	28 424.82	28 428.62	28 431.02	28 755.73	28 658.93
6	28 672.23	28 689.63	28 691.43	28 892.64	28 768.53
$7h$	28 762.13	28 780.53	28 781.73	28 945.14	28 816.54
$8h$	28 819.34	28 824.04	28 824.94	28 967.24	28 835.64
$9h$	28 846.64	28 851.74	28 852.84	28 978.64	28 845.74
${}^2P^o$					
N	74 103	74 103	158 337	35 919	35 919
E	-24.65289	-24.65286	-24.65290	-24.61069	-24.62290
4P					
N	50 095	50 095	113 935	25 250	25 250
E	-24.52145	-24.52141	-24.52144	-24.47856	-24.49147

with n . In order to test the dependence of the final answers on the MR set, calculation [C] repeated the simultaneous optimization, starting with an $n = 3$ MR set that included SDTQ excitations from all shells. Though the expansions are much larger, the final excitation energy is only 1.10 cm^{-1} larger and the total energies less than $4.0 \times 10^{-5} E_h$ lower than calculation [B]. The radii for all the $9l$ optimized orbitals of the $n = 9h$ layer calculation were CC orbitals as well as some of the $8l$ orbitals, showing orbital dependence on all three types of correlation.

In calculation [D], the CSFs with an unoccupied $1s$ shell were omitted from the expansion, unless the remaining shells consisted only of $2s, 2p$ electrons, thereby neglecting CC correlation outside the $n = 2$ complex. Simultaneous optimization was applied. The occupied orbitals ($1s, 2s, 2p$) were obtained from a small MCHF calculation and then kept fixed. The final $n = 9h$ result is similar to the Tachiev and Froese Fischer [4] value and because the correlation that is included is over a smaller region of space, the convergence with respect to the orbital set is rapid. The fully variational results with the same expansion, and simultaneous optimization (calculation [E]), had the most convergence problems of any method. A considerable transformation of the orbitals occurred, and it was important not to require that the $1s, 2s, 2p$ orbitals be spectroscopic orbitals with the usual nodal structure. In particular, the final $1s$ orbital was contracted and, in the screened hydrogenic model, had a screening parameter of -0.14 . The final excitation energy, however, was in excellent agreement with the independently optimization results.

Table I also specifies the size (N) of the ($9h$) wave function expansions for each calculation. Those without core correlation ([D] and [E]) have much smaller wave function expansions, a fact that is important in atoms with a large core. The total energy of each strategy is reported as well. Omitting CC raises the total energy significantly but the effect on the excitation energy is much smaller. This table clearly indicates that the correct excitation energy is closer to the Edlén *et al.* value than the Kramida and Ryabtsev one.

Extending the MCHF method to higher accuracy would require a rather large set of orthonormal orbitals since orbitals

with higher angular quantum numbers should also be included. An alternative is to introduce the use of nonorthogonal orbitals.

III. THE PARTITIONED-CORRELATION-FUNCTION INTERACTION

The partitioned-correlation-function-interaction (PCFI) method that has been described in detail elsewhere [12,13], differs from the MCHF method in that the correction to the wave function Ψ_0 of the MR space is partitioned so that different orbital bases can be used for different correlation effects.

In this method the correction to the wave function for three types of correlation is a linear combination of partitioned correlation functions (PCFs), denoted by P_i , so that

$$\Psi_1 = c_1 P_1 + c_2 P_2 + c_3 P_3. \quad (2)$$

Each P_i is itself a linear combination of CSFs, where the expansion coefficients and the orbitals are an MCHF solution for the wave function $\Psi_0 + P_i$, with the orbitals of Ψ_0 fixed. Because the MCHF method requires a single orthonormal basis, the new orbitals for each partition P_i must be orthogonal to the orbitals defining Ψ_0 , but may be nonorthogonal to those from other partitions. For the present case, the partitions represent VV, CV, and CC correlation corrections, respectively. Biorthogonal methods are then used to compute the interaction matrix in a nonorthogonal basis for a wave function expanded in the CSF basis defining Ψ_0 , and the partitions P_1, P_2, P_3 . Some variational freedom is lost by this method since the expansion coefficients for each partition can now only be scaled by a constant factor. In order to recover full variational freedom in the expansion coefficients, a deconstraining procedure may be applied in which, when forming the PCFI configuration interaction matrix, a configuration state function is moved from a partition into the set defining Ψ_0 [13].

A. Nonrelativistic calculations for boron

The same MR sets as used for the MCHF study were adopted. Applying the SD process to each set, the resulting

TABLE II. Nonrelativistic total energies, E in E_h , and excitation energy, ΔE in cm^{-1} , of the lowest $^2P^o$ and 4P terms of neutral boron obtained with the PCFI and DPCFI method. The total energies for a DPCFI calculation are reported as $10D$ and the excitation energy as $\Delta E(D)$.

n	$E (^2P^o)$	$E (^4P)$	ΔE	$\Delta E(D)$
4	-24.644 046 909	-24.514 398 526	28 454.53	28 457.66
5	-24.650 782 918	-24.519 740 851	28 760.40	28 765.41
6	-24.652 391 314	-24.520 979 432	28 841.57	28 847.00
7	-24.652 978 136	-24.521 441 671	28 868.91	28 875.86
8	-24.653 244 882	-24.521 636 963	28 884.59	28 890.74
9	-24.653 383 550	-24.521 735 733	28 893.35	28 899.63
10	-24.653 464 335	-24.521 792 201	28 898.69	28 905.08
$10D$	-24.653 523 595	-24.521 822 334		28 905.08
E^{exact} [9]	-24.653 93			

expansions were classified according to the occupation number of the $1s$ shell. For each state, the next step was to obtain the orbitals for Ψ_0 . Keeping these orbitals frozen, MCHF calculations were performed for each of their three partitions. Because the orbital basis now targets the same type of correlation, there is less rearrangement of orbitals as new layers of orbitals are added, so that convergence is better and calculations can readily be extended to $n = 10$ without any truncation of the angular quantum numbers.

Using the resulting PCFs, the configuration interaction matrix was built. Table II displays the total energies and excitation energy calculated with the original constrained representation of each PCF. The energies of the $n = 9$ results are significantly lower than the MCHF results of Table I.

To check the sensitivity of the excitation energy to the constraint effect, we also report results from the deconstrained partitioned-correlation-functions-interaction (DPCFI) method, where all the expansion coefficients are free to vary. The modified excitation energy is included in Table II in the last column and denoted as $\Delta E(D)$. The final total energies and excitation energy are presented as $n = 10D$ results. From these data we see that the deconstraint increases the excitation energy by 6.39 cm^{-1} . The changes are small but bring the total energy into better agreement with the exact nonrelativistic energy [9] for the ground state.

The effect of increasing the MR set was also evaluated, using the complete active space (CAS) concept for a valence correlation expansion of Ψ_0 for each of the two states, namely

$$\begin{aligned}
 1s^2 2s^2 2p^2 P^o &: 1s^2 \{2s, 2p, 3s, 3p, 3d\}^3 {}^2 P^o, \\
 1s^2 2s 2p^2 {}^4 P &: 1s^2 \{2s, 2p, 3s, 3p, 3d\}^3 {}^4 P.
 \end{aligned} \quad (3)$$

This notation represents an expansion over CSFs from configurations with a $1s^2$ core and three orbitals of the required symmetry and parity for the given list of orbitals. The MR expansions contain 30 and 13 CSFs for the odd and even parity, respectively. Allowing single and double excitations from these CSFs we get the CSF space that was partitioned into the three PCFs (VV, CV, and CC). The expansion size grows rapidly – 242 532 and 175 542 for $^2P^o$ and 4P , respectively, for $n = 9$ and 357 230 and 258 565 for $n = 10$. However, with

partitioning the expansion into three parts, the final size is computationally feasible.

Systematic calculations can be improved through extrapolation of trends to $n = \infty$, which in our procedure also implies $l = \infty$. MCHF convergence trends have been investigated by Tong *et al.* [17] where results are extrapolated first by n , as a function on the maximum l , and then for l . The rate of convergence of the former for a given maximum l is more rapid than for l . For helium, Schwartz [18] showed that the contribution from higher orbital angular momenta was proportional to $1/l^4$ for symmetric states and $1/l^6$ for antisymmetric. For this angular type of asymptotic behavior, the rate of convergence $(E_{l+1} - E_l)/(E_l - E_{l-1})$ approaches unity.

In the present work, a much simpler procedure has been used to estimate the remaining uncalculated contribution, a procedure that underestimates the correction. To perform the extrapolation, we consider the change in energy (or excitation energy) $\delta E_9 = E_9 - E_8$ and $\delta E_{10} = E_{10} - E_9$ to determine the rate of convergence:

$$r = \delta E_{10}/\delta E_9. \quad (4)$$

If we assume that the convergence continues at the same rate for the rest of the sequence, the remainder is a geometric series that can be summed to yield

$$\sum_{i=1}^{\infty} \delta E_{10} r^i = \delta E_{10} \frac{r}{1-r} \quad \text{if } |r| < 1. \quad (5)$$

In fact, the ratio increases with n because of the slow convergence of contributions from the higher angular momenta.

B. Relativistic and finite mass corrections

For a light atom, relativistic effects can be accurately estimated in the Breit-Pauli approximation. The terms of the Breit-Pauli operator can be classified into the J -dependent fine-structure (FS) and LS -dependent relativistic shift (RS) contributions [14]. For boron, the latter are the more important corrections and were easily included in this extensive calculation.

Table III presents the total energies of each state as well as the excitation energies obtained using the PCFI method with a Hamiltonian including the relativistic shift operators. For the purpose of comparison, excitation energies from the smaller calculations of Table II that also include the relativistic shift operators are reported in the last column and are denoted as $\Delta E(S)$. The increase in the excitation energy of 2.26 cm^{-1} is in agreement with the small increase observed in the MCHF calculations reported in Table I when including higher-order excitations ($[B] \rightarrow [C]$). The RS contribution to the doublet-quartet excitation energy is estimated to be the difference between the $n = 10$ values of $28\,942.06$ [$\Delta E(S)$ of Table III] and $28\,898.69$ (ΔE of Table II), or 43.37 cm^{-1} .

Table IV reports the excitation energy using the complete Breit-Pauli Hamiltonian within the PCFI approach. LS -term mixing of different terms is omitted. Subtracting the $\Delta E(S)$ values reported in Table III from the Breit-Pauli ΔE values of Table IV, we get an estimate of the importance of the LS diagonal fine-structure operators, i.e., -0.74 cm^{-1} . Comparing

TABLE III. PCFI total energies, E in E_h , and excitation energy, ΔE in cm^{-1} , including the relativistic shift operator, of the lowest ${}^2P^\circ$ and 4P terms of neutral boron. The MR set included all CSFs of $1s^2\{2s,2p,3s,3p,3d\}^3$ of the required symmetry and parity. $\Delta E(S)$ refers to the excitation energy including the relativistic shift operator from calculations with the smaller MR of Table II. N is the size of the $n = 10$ CSF expansion.

n	$E({}^2P^\circ)$	$E({}^4P)$	ΔE	$\Delta E(S)$
4	-24.650 382 640	-24.520 438 740	28 519.38	28 496.83
5	-24.657 117 561	-24.525 847 143	28 810.52	28 803.21
6	-24.658 725 942	-24.527 084 872	28 891.87	28 885.02
7	-24.659 297 417	-24.527 551 340	28 914.92	28 912.18
8	-24.659 568 315	-24.527 751 544	28 930.43	28 927.90
9	-24.659 709 842	-24.527 853 807	28 939.05	28 936.71
10	-24.659 792 829	-24.527 912 772	28 944.32	28 942.06
∞	-24.659 910	-24.527 993	28 952.52	
N	357 230	258 565		

the ΔE and $\Delta E(D)$ values in Table IV reveals the constraint effect on the excitation energy in the BP approximation, i.e., 7.05 cm^{-1} , which differs somewhat from the earlier estimate of 6.39 cm^{-1} . The difference of 0.66 cm^{-1} is small and establishes a lower limit on the uncertainty of our procedure. Thus not all corrections are first-order effects, although the difference is less than 1.0 cm^{-1} .

The finite-mass correction should also be considered. The normal mass (NMS) correction can readily be determined from the Bohr mass scaling law, using the finite-mass Rydberg constant. This reduces the excitation energy by -1.59 and -1.44 cm^{-1} for ${}^{10}\text{B}$ and ${}^{11}\text{B}$, respectively. However, for the excitation energy under consideration the specific mass shift is larger than expected. Using the $n = 10$ PCFI wave functions for estimating the ΔS_{sms} difference of the specific mass shift parameters [19], the finite mass (NMS+SMS) corrections are

$${}^{10}\text{B}: -6.67 \text{ cm}^{-1} \quad \text{and} \quad {}^{11}\text{B}: -6.07 \text{ cm}^{-1}.$$

The deconstraint correction on ΔS_{sms} is very small and an average over the two isotopes based on the natural isotopic composition (19.9% ${}^{10}\text{B}$ /80.1% ${}^{11}\text{B}$) gives a final estimation of -6.20 cm^{-1} . This correction is therefore important for spectroscopic accuracy.

TABLE IV. Breit-Pauli total energies, E in E_h , and corresponding excitation energy, ΔE in cm^{-1} , of the lowest ${}^2P_{3/2}^\circ$ and ${}^4P_{5/2}$ levels of neutral boron using both the PCFI and DPCFI methods.

n	$E({}^2P_{3/2}^\circ)$	$E({}^4P_{5/2})$	ΔE	$\Delta E(D)$
4	-24.650 251 936	-24.520 414 146	28 496.10	28 499.14
5	-24.657 033 103	-24.525 799 428	28 802.46	28 807.83
6	-24.658 656 372	-24.527 049 905	28 884.28	28 890.09
7	-24.659 251 843	-24.527 521 599	28 911.44	28 918.01
8	-24.659 523 392	-24.527 721 520	28 927.16	28 933.87
9	-24.659 666 371	-24.527 824 368	28 935.97	28 942.94
10	-24.659 749 687	-24.527 883 327	28 941.32	28 948.37
∞			28 949.56	28 956.47
10D	-24.659 913 687	-24.528 015 185		28 948.37

TABLE V. Total energies, E in E_h , and excitation energy, ΔE in cm^{-1} including the relativistic shift operator, of the lowest ${}^2P^\circ$ and 4P terms of the singly ionized carbon atom obtained using the PCFI method as well as some DPCFI excitation energies. Observed data have been obtained from an LS spectrum (see text).

n	$E({}^2P^\circ)$	$E({}^4P)$	ΔE	$\Delta E(D)$
4	-37.434 442 461	-37.241 016 132	42 452.17	42 454.33
5	-37.441 661 608	-37.246 648 961	42 800.32	42 804.62
6	-37.443 459 176	-37.247 990 596	42 900.39	42 905.57
7	-37.444 132 978	-37.248 491 723	42 938.29	42 944.35
8	-37.444 453 444	-37.248 717 425	42 959.09	
9	-37.444 620 358	-37.248 830 141	42 970.98	
10	-37.444 721 702	-37.248 898 421	42 978.24	
∞	-37.444 878	-37.249 003	42 989.59	
Deconstraint			7.05	
Finite mass			-10.22	
Excitation energy			42 986.42	
Young <i>et al.</i> [20]			42 993.0 \pm 0.9	
ASD [3]			42 993.5	

C. The C II quartet-doublet energy separation

In order to estimate the errors not accounted for, mainly the contributions from orbitals with high-angular quantum numbers, we validate our method by applying it to the calculation of the excitation energy in C II where the wavelength of the ${}^2P_{3/2}^\circ - {}^4P_{5/2}$ transition has been measured recently by Young *et al.* [20] and ASD [3] values are available.

For maximum accuracy we start with the valence CAS expansion to determine Ψ_0 and then the PCFs for the three types of correlation. In generating the configuration interaction matrix we used the Breit-Pauli Hamiltonian but with only the relativistic shift operators, because of the size of the expansion and the small effect from the J -dependent terms.

Table V reports the results for C II. Because of the large expansions, deconstrained DPCFI excitation energies are not included for the higher layers, but the effects of deconstraining closely track those of Table IV where the final difference was 7.05 cm^{-1} . The finite mass correction for an isotopically unresolved line profile, is largely dominated by the lightest isotope (98.93% ${}^{12}\text{C}$ /1.07% ${}^{13}\text{C}$) and is estimated to be -10.22 cm^{-1} . Correcting the extrapolated $n = 10$ results in Table V by these amounts we get $42 986.42 \text{ cm}^{-1}$. Comparing this value with excitation energies derived from observed data by defining each term energy to be the statistically weighted average of the levels of the term, we get a remainder of 6.58 cm^{-1} representing residual correlation and other omitted effects that were not captured in our calculation for C II.

D. Final estimate for the $2s^2 2p \ {}^2P_{3/2}^\circ - 2s 2p^2 \ {}^4P_{5/2}$ excitation energy in B I

The results of our investigation of the various aspects of the PCFI method as applied to the $2s^2 2p \ {}^2P_{3/2}^\circ - 2s 2p^2 \ {}^4P_{5/2}$ excitation energy are summarized in Table VI. Listed are the contributions to the energy starting with the nonrelativistic PCFI value of Table II based on the small MR list. Since the corrections are small, values of contributions were obtained by expressing the $n = 10$ excitation energies of Tables II–IV

TABLE VI. Summary of contributions to the $2s^22p\ 2P_{3/2}^o - 2s2p^2\ 4P_{5/2}$ excitation energy (in cm^{-1}) in B I.

Excitation energy [PCFI(MR)]	28898.69
Relativistic shift (RS)	43.37
Fine-structure (FS)	-0.74
Deconstraint (D)	7.05
Extrapolation (X)	8.10
Larger MR set (CAS)	2.26
Finite mass	-6.20
Remainder (same as for C II)	6.58
Total excitation energy	28959 ± 5
Edlén <i>et al.</i> [1]	28866 ± 15
Kramida and Ryabstev [2]	28643.1 ± 1.8

in terms of the PCFI value and contributions, assuming a first-order theory. As mentioned earlier, in some instances, a contribution (such as D) could have two slightly different values, in which case it was determined from a calculation that included the most corrections in a given calculation. In fact, the sum of the first five entries is the extrapolated value of Table IV that includes the deconstraining correction. Our method of computing the correlation energy has accounted for the terms linear in Z of a Z -dependent calculation. Hence, remaining correlation in B I should be similar to that in C II. The uncertainty estimate largely represents the uncertainty of our estimate of the remainder.

Thus our prediction for the $2s^22p\ 2P_{3/2}^o - 2s2p^2\ 4P_{5/2}$ excitation energy is $28959\ \text{cm}^{-1} \pm 5\ \text{cm}^{-1}$, considerably larger than the Edlén *et al.* value of $28866 \pm 15\ \text{cm}^{-1}$ and the Kramida and Ryabstev value of $28643.1\ \text{cm}^{-1}$.

IV. CONCLUSION

The MCHF and PCFI methods have been combined to extend the accuracy of variational methods for complex atoms and ions. In this case, near spectroscopic accuracy has been attained. Extrapolating the excitation energies along the isoelectronic sequence to estimate its value for the neutral atom appears to be unreliable. The “divide and conquer” strategy used in the (D)PCFI method of partitioning the correlation space in order to capture electron correlation more efficiently is confirmed to be an attractive computational approach.

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