New bound state of the negative B ion

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The lowest septets of B^- associated with configurations $1s2s2p^23s3p$ and $1s2s2p^23p^2$ have been explored, including the effects of electron correlation, and one new bound state, the ^7S, having an affinity of 0.0857 eV, has been found. As the state decays primarily by radiative autoionization, it may be a candidate for lasing activity.

Recently,[1–4] several studies of the excited discrete spectra (by discrete, we mean the state lies below all nonrelativistically relevant thresholds) of small negative ions, including H^-, H^{2-}, He^-, Li^-, and Be^-, have become available, and six new states have been predicted to be bound. The two Li^- states[3] have been experimentally detected,[5] and the $2p^3\,^4S^0$ state of He^-,[1,2] as well as the three states[4] of Be^-, are the focus of current experimental interest. Excited states of negative ions may be of unusual interest because they have the potential to decay principally via the mechanism of radiative autoionization,[6] during which an electron and photon are simultaneously emitted over a fairly broad frequency range. This feature, combined with a possible population inversion due to the nature of the lower states, led to the suggestion[7] that these species might be used to construct tunable atomic lasers, some of which (e.g., He^-) might operate in the x-ray region.

In this work, we extend our study to B^-. Two bound states are already known to exist: B^- $1s^22s^22p^2\,^3P$ with a measured[8] electron affinity (E.A.) of 0.28 eV, which has also been theoretically estimated[9] as 0.24 eV, and B^- $1s^22s2p^3\,^5S^0$ with a calculated[10] E.A. of 0.89 eV.

In surveying negative ion spectra to find which states we should focus our computational efforts on, two observations are used: (1) The least bound electron should not singly occupy a shell or, preferably, even a subshell. Redistribution of the "core" electrons can be used to avoid this, if possible; (2) The energetically highest thresholds often occur for the highest multiplicity S states. A contrary trend is that such S states are least likely to be bound in the restricted Hartree-Fock (RHF) approximation. Consistent with these observations, the threshold for $1s^22s2p^3\,^{1,3}PD^0$ is $1s^22s^22p$, making it unlikely these are bound, whereas the threshold for $1s^22s2p^3\,^{3,5}S^0$ is $1s^22s2p^2\,^4P$, although only the $^5S^0$ is bound,[10] as the $^3S^0$ is about 7.5 eV higher than the $^5S^0$ at the RHF level.

Since it appears that occupation of just the $1s$, $2s$, and $2p$ subshells offer no other likely candidates (e.g., B^- $1s^22s^22p^2\,^1D$ seems[11] to be unstable by about 0.38 eV), we turned our attention to occupancies involving the $3s$ and/or $3p$ subshells, as this allows formation of the lowest septets of this species. Specifically, B^- $1s2s2p^23s3p$ forms $^7SPD^0$ and B^1 $1s2s2p^23p^2$ forms ^7SPD. But $1s2s2p^3\,^6S^0$ acts as a threshold for $^7SD^0$ and ^7P, thus making it unlikely that these are bound.

The remaining three terms were initially explored at the RHF level, using the code of Froese-Fischer.[12] The ^7D RHF energy was $-17.287\,360\,9$ a.u. or about 1 eV above the RHF threshold energy for B $1s2s2p^23s\,^6P$ which is $-17.323\,152\,2$ a.u. Since it is unlikely that there is this much differential correlation energy between the two states (most of which would reside in the $3p^2$ pair, i.e., about 0.2 eV), it is unlikely the ^7D is bound. RHF calculations for the $^7P^0$ were not obtained below $Z=5.1$ because the $3p$ orbital becomes too diffuse. Instead, the configuration interaction (CI) result for $Z=5.0$ was obtained using the RHF functions for $Z=5.1$ and correlating the $3s3p$ pair and including various polarization functions (this method can be used to produce RHF solutions[13]), but it was found that the $^7P^0$ was about 0.25 eV above the ^6P threshold. Since the bulk of the differential correlation contribution has been included, it appears that this state is unbound as well.

The remaining state ^7S is only nonbound by 0.069 eV at the RHF level, so this state and its threshold, B $1s2s2p^23p\,^6P^0$, were carefully correlated. All single, double, and selected triple and quadruple subshell excitations from the K, L, and M subshells into all available (HF + virtual) one-electron functions were examined for both states.

We generated the virtual functions by first performing symmetry adapted independent pair approximation (SA/IEPA) calculations[13] on the LL (LM,MM,KL,KM) portions of the CI space. This provided us with initial estimates of the exponents and powers of the Slater-type orbitals (STO's) used in the full CI calculation. Generally, these calculations involved three separately optimized STO's for each of the s, p, d, f symmetries.

Full CI calculations for each of the states were then performed by first forming single and double subshell

excitations of the RHF function (yielding E_{S+D}), by using at least the two most important SA/IEPA virtuals (per symmetry/per section) whose exponents were reiterated. Only terms with coefficients greater than 0.001 or energy contributions larger than 0.01 millihartrees were kept. The $S+D$ functions were then augmented by triple and quadruple (for ^7S) excitations, yielding the final $S+D+T+Q$ results, which were formed from the larger single and double excitations. The results, shown in Table I, yield an E.A. of 0.0857 eV, to which quadruples contribute 0.016 eV.

By using the final matrices, we produced another set of SA/IEPA results (simply striking out nonrelevant matrix elements) and compared these to the ones obtained originally to check the completeness of the virtual space. The difference between the ^7S, $^6P^0$ energy difference obtained in these two ways was found to be 0.005 eV, which was used to estimate an error in the E.A. of 0.01 eV. The total energies, based on the above analysis, should have about twice this error. It should also be noted that the effects of relativity are assumed to be identical for both states.

Since there appears to be no bound $^7P^0$, the ^7S decays primarily via nonrelativistic radiative autoionization, viz.,

$$1s2s2p^23p^2{}^7S \rightarrow 1s2s2p^23s\epsilon p\,{}^7P^0 + h\nu \ ,$$

TABLE I. Energetics for B^- ^7S and B $^6P^0$.

	B^- $1s2s2p^23p^2{}^7S$	B $1s2s2p^23p\,{}^6P^0$
E_{RHF} (a.u.)	−17.284 803 53	−17.287 332 56
E_{S+D}[a] (a.u.)	−17.314 423 53	−17.312 078 01
E_{S+D+T}[a] (a.u.)	−17.314 638 96	−17.312 085 69
$E_{S+D+T+Q}$ (a.u.)	−17.315 239 93 (175 vectors)	−17.312 985 69 (118 vectors)
E.A. (eV)	0.0857	

[a] E_{S+D} was obtained from the final CI matrix by removing all triple and quadruple excitations. For E_{S+D+T} only the quadruple excitations were dropped.

emitting photons up to 0.89 eV in energy (we used the RHF approximation to estimate the $1s2s2p^23s\,{}^6P$ to $1s2s2p^23p\,{}^6P^0$ gap). It shoud be noted that photons of this energy can be obtained from existing lasers, unlike the He^- system[7] which can involve 38-eV photons.

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