Spectrum of the negative Be ion

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The existence of Be^- is established from electron correlation calculations which include one-, two-, three-, and four-orbital excitations. The discrete spectrum of Be^- consists of three states: $1s^2 2s 2p^2 \, ^4P$, $1s^2 2p^3 \, ^4S^o$, and $1s\,2s\,2p^3 \, ^6S^o$. The $^4S^o$-^4P transition offers the possibility of experimental detection of Be^-, e.g., by beam-foil methods. The theoretical wavelength and probability for the transition are $\lambda = 2671$ Å and $A = 0.67 \times 10^9 \, \text{sec}^{-1}$, respectively.

Negative ions constitute unusual states of matter whose experimental and theoretical study is of current interest for a number of reasons.[1,2] In the past, the normal research activities dealt with the ground states of such species and the question of their electron affinities. One of the few early results for excited discrete states was that of Drake,[3] for $H^- \, 2p^2 \, ^3P$.

Recently,[4-8] accurate theoretical predictions have appeared which provided the first well-founded information about the discrete spectra of H^{2-}, H^-, He^-, and Li^-. The prediction[4] of the two Li^- excited states has now been experimentally verified.[9] Similarly, the prediction[7] of the He^- $2p^3 \, ^4S^o$ bound state and the clarification[8] in the He^- spectrum as to the nature of the $1s\,2p^2 \, ^2P, \, ^4P$ configurations (they correspond to core excited *shape* resonances and not to bound states), has led to the suggestion[10] of the possibility of constructing tunable atomic lasers of high frequency by utilizing the process of radiative autoionization.[11]

In this note, we report the first determination of the Be^- discrete spectrum which is found to consist of three states: $1s^2 2s\,2p^2 \, ^4P$, $1s^2 2p^3 \, ^4S^o$, and $1s\,2s\,2p^3 \, ^6S^o$. The ground state of Be is $1s^2 2s^2 \, ^1S$ for which the addition of an electron ($2p$ shell) yields an unbound system, $Be^- \, 1s^2 2s^2 2p \, ^2P^o$, which might manifest itself as a shape resonance.[12] No bound states have been predicted before.

In predicting possible bound states of negative ions, spin and symmetry considerations together with the spectra of the neutral atoms suggest the configurations of the ions which could correspond

to bound states. In the case of Be^-, analysis shows that the configurations $1s^2 2s\,2p^2 \, ^4P$, $1s^2 2p^3 \, ^4S^o$, and $1s\,2s\,2p^3 \, ^6S^o$ can correspond to bound states provided they lie below the Be $1s^2 2s\,2p \, ^3P^o$, $1s^2 2p^2$ ^3P, and $1s\,2s\,2p^2 \, ^5P$ excited states correspondingly (as was noted in Ref. 8). The positions of the triplet states with respect to the ground state—and therefore their total energies—are well established from optical spectra.[13] The Be ^5P state has been observed in emission from the $1s\,2p^3 \, ^5S^o$ state[9,14] (λ = 1909 Å) but its total energy is experimentally unknown (it would require the measurement of an energy difference from a state of known total energy, i.e., Be lower-lying states or Be positive ions). Thus, we have computed four total energies: Be^- $1s^2 2s\,2p^2 \, ^4P$, $1s^2 2p^3 \, ^4S^o$, $1s\,2s\,2p^3 \, ^6S^o$, and Be $1s\,2s\,2p^2 \, ^5P$ of which the first two were compared with the experimental values for Be $1s^2 2s\,2p \, ^3P^o$ and $1s^2 2p^2 \, ^3P$.

We outline briefly our computational approach. A longer paper[15] will contain the details. A recent review of our methods is given in Ref. 16.

We start with a Hartree-Fock function obtained numerically from Froese-Fischer's code.[17] We then construct one-, two-, three-, and four-orbital symmetry adapted correlation functions. These functions are expressed in terms of Slater-type orbitals (STO's) whose exponent variational optimization is initialized using overlap and first-order perturbation theory criteria.[15,16] The final results were obtained from a total CI containing only those optimized correlation vectors which contribute more than 0.001 eV and/or have expansion coefficients

TABLE I. Energetics required to predict electron affinities of the three bound states of Be⁻.

| | Be⁻ | | | | Be | |
	$1s^2 2s\, 2p^2$ ^4P	$1s^2 2p^3$ $^4S^o$	$1s\, 2s\, 2p^3$ $^6S^o$	$1s^2 2s\, 2p$ $^3P^o$	$1s^2 2p^2$ ^3P	$1s\, 2s\, 2p^2$ ^5P
E_{HF} (a.u.)	$-14.509\,028$	$-14.327\,52$	$-10.428\,833$			$-10.400\,04$
E_{S+D} (a.u.)	$-14.569\,93$	$-14.397\,529$				
E_{S+D+T} (a.u.)	$-14.570\,07$	$-14.398\,612$				
$E_{S+D+T+Q}$ (a.u.)	$-14.570\,77$	$-14.400\,170$	$-10.461\,51$			$-10.417\,27$
E_{exp} (a.u.)				-14.5683[a]	-14.4006[a]	
$\epsilon_{E.A.}$ (eV)	>0.122	$>0.042\,7$	1.20			

[a]To obtain this number, we used the total energy (Ref. 19) for the ground state ($-14.668\,45$) of Be, removed the relativistic contribution (Ref. 19) ($-0.001\,987$ a.u.), and added the experimentally observed (Ref. 13) optical transition energy.

larger than 0.0005.

For the Be⁻ $1s^2 2s\, 2p^2$ ^4P and $1s^2 2p^3$ $^4S^o$ states, comparison of relativistic Hartree-Fock energies using Desclaux's code[18] with nonrelativistic HF energies yielded a relativistic correction for Be²⁺ $1s^2$ of $-0.002\,08$ a.u. However, in order to be more conservative we used Bunge's estimate[19] for Be $1s^2 2s^2$ ^1S of $-0.001\,987$ a.u. In the case of Be⁻ $1s\, 2s\, 2p^3$ $^6S^o$ and Be $1s\, 2s\, 2p^2$ ^5P, whose total energies were predicted theoretically and then subtracted, relativistic contributions were assumed to cancel.

The results of our calculations are presented in Table I. The rows E_{S+D}, E_{S+D+T}, and $E_{S+D+T+Q}$ correspond to the total CI energies with single and double; single, double, and triple; and single, double, triple, and quadruple subshell excitations. The quadrupole contributions were computed by setting to zero all off-diagonal matrix elements involving quadruples of the total CI (S+D+T+Q) energy matrix, and then rediagonalizing. To obtain the triple contributions, triple and quadruple off-diagonal matrix elements were set to zero for this matrix. We believe that $E_{S+D+T+Q}$ is accurate[15] to $0.05-0.06$ eV for the $^4S^o$, ^4P states (Ref. 15 will contain more details). The wavelength for the $^4S^o \rightarrow ^4P$ transition is probably good to $0.01-0.02$ eV. Errors for the total energies of ^5P and $^6S^o$ are probably twice those for $^4S^o$, ^4P. We note that $^6S^o$ is bound already in the Hartree-Fock approximation, whereas for ^4P and $^4S^o$ consideration of electron correlation is necessary.

How do the three bound states of Be⁻ decay? The $1s^2 2p^3$ $^4S^o$ decays radiatively to the ^4P. We have computed the wavelength to be $\lambda = 2671$ Å and the transition probability $A = 0.67 \times 10^9$ sec⁻¹. The lifetime of $^4S^o$ is shorter than $1/A$ by

$10-15\%$ due to radiative autoionization.[10] The ^4P and $^6S^o$ are nonrelativistically completely stable. However, introduction of relativistic operators induces the following decay processes.

(1) For ^4P, relativistic autoionization (REA) into the Be $1s^2 2s^2$ $^1S + e^-$ (^2S, ^2D) continuum as well as relativistic radiative autoionization[8,10,11] (RRA) into the Be $1s^2 2s^2$ $^1S + \epsilon p$ ($^2P^o$) continuum is allowed. Given the fast decay $^4S^o \rightarrow ^4P$, we expect that in processes where these states are excited (e.g., see case of Li⁻ states[9]), the population of ^4P will become sufficiently large to create practical conditions of population inversion with respect to the adjacent continuum and possible subsequent induced emission of continuous coherent radiation.[10]

(2) For $^6S^o$, REA and RRA into the Be $1s^2 2s\, 2p$ $^3P^o + e^-$ continuum as well as a quasidiscrete transition to the ^4P state are allowed. At present, quantitative results for these unusual processes are not available.

Finally, it is worth pointing out that, because of symmetry restrictions, the wave functions of negative ion bound states as well as of the corresponding neutral states do not include any "hole-filling" electron correlations.[16,20,21] Such correlations affect the character of the wave function considerably and contribute to the instability of excited states in the continuum. An example of both cases can be found in the B spectrum[22] which is isoelectronic with Be⁻. Another example of such spin and symmetry constraints is the $2p^3$ configuration of He⁻. The $^2P^o$ symmetry allows hole-filling and Fermi-Sea correlations, which cause autoionization of the He⁻ $2p^2$ $^2P^o$ state predicted to be at about 60.5 eV above He $1s^2$ ^1S.[23] On the other hand, the $^4S^o$ symmetry allows only bivirtual and higher excitations which contribute only to the stability of the

system and are sufficient to make it bound.[7,8] In general, lack of hole-filling correlation effects for states in the continuum will allow the existence of a bound state or of a core excited shape resonance. In both cases, the Hartree-Fock function describes the state reasonably well.[8,11]

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