Duguay and Rentzepis[10] for pumping an x-ray laser by photoionization to selectively populate certain inner-shell vacancy states is based on similar principles. In selective autoionization, it is the dynamics of the two-electron interaction which leads to the selective decay of a doubly excited autoionizing state to the desired ion continuum. Selective autoionization thus represents a qualitatively new physical mechanism for the production of population inversions in ions. From a practical point of view, direct photoionization and selective autoionization are complementary in that the former is well matched to a broadband optical pumping source, while selective autoionization requires a relatively narrowband pump source. Sources such as direct multiphoton laser excitation (as demonstrated here) and spontaneous anti-Stokes Raman scattering[11] might be used to pump new selective autoionization lasers.

In summary, selective autoionization has been demonstrated as a new physical principle for the production of population inversion and laser action in atomic ions. Since the phenomenon of selective autoionization has been observed in several inner-shell excited atoms[2-6] it is believed to be quite general. We therefore anticipate the construction of a new class of optically excited ion lasers operating in the deep ultraviolet region of the spectrum.

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Correlation and Relativistic Effects in Spin-Orbit Splitting

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A large discrepancy between Dirac-Fock calculations and experiment for the spin-orbit splitting, $^2P_{1/2}$-$^2P_{3/2}$, in the ground states of B- and F-like ions is resolved. The discrepancy arises from spurious terms which are inherent in the relativistic self-consistent-field procedure. Removal of these terms substantially improves the agreement between theory and experiment on spin-orbit splitting.

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Forbidden transitions with wavelengths in the visible and uv region are of interest to astrophysics because they are convenient to study experimentally.[1] More recently, for the same reason, the magnetic dipole transitions between spin-orbit-split levels of highly stripped ions have become an indispensable tool for plasma diagnostics in fusion devices.[2]

In a systematic study of energy levels for stripped ions, we noticed a large discrepancy between the Dirac-Fock calculations[3] and experiment on the spin-orbit splitting, $^2P_{1/2}$-$^2P_{3/2}$, in

the ground states of B- and F-like ions of low ionicity. The Dirac-Fock wave functions and associated energy levels are calculated from the usual self-consistent-field (SCF) procedure with the Dirac Hamiltonian.[4] Contributions from the Breit interaction and the Lamb shift are also included.

The ground-state configurations of a B-like ion are $(2s^2 2p_{1/2})\,^2P_{1/2}$ and $(2s^2 2p_{3/2})\,^2P_{3/2}$, where the K-shell core is omitted for brevity. To account for the most important electron correlation, we include all configurations within a complex[5] that have the same total angular momentum and parity. In the LSJ notation, multiconfiguration representations of the ground-state levels can be written as

$$(2s^2 2p)\,^2P_{1/2} + (2p^3)\,^2P_{1/2} \tag{1}$$

for $^2P_{1/2}$, and

$$(2s^2 2p)\,^2P_{3/2} + (2p^3)\,^2P_{3/2} + (2p^3)\,^4S_{3/2} + (2p^3)\,^2D_{3/2} \tag{2}$$

for $^2P_{3/2}$. Single-configuration calculations include only the first term on the right-hand side of Eqs. (1) and (2). The spin-orbit splitting between the two ground levels, $^2P_{1/2}$ and $^2P_{3/2}$, is of relativistic origin but is modified by electron correlation. For F-like ions, the situation is different. Within the ground-state complex, only one configuration is possible for each fine-structure level: $(2s^2 2p^5)\,^2P_{1/2}$ and $(2s^2 2p^5)\,^2P_{3/2}$.

In Table I we present selected single-configuration and multiconfiguration results on the spin-orbit splitting and compare them with known experimental data. In principle the multiconfiguration results should be better than the single-configuration ones because correlation effects are treated better by the multiconfiguration procedure. In practice, however, we notice a large discrepancy between the previous multiconfiguration Dirac-Fock calculations and experiment for B-like ions of low ionicity, while the single-configuration results agree well with experiment. To understand this apparent contradiction, let us write formally the total energies of the fine-structure levels as functions of the nuclear charge Z and the fine-structure constant α:

$$E(^2P_{1/2}) = u_{1/2}(Z) + \alpha v_{1/2}(Z,\alpha), \tag{3}$$

$$E(^2P_{3/2}) = u_{3/2}(Z) + \alpha v_{3/2}(Z,\alpha). \tag{4}$$

The second term on the right-hand side of Eqs. (3) and (4) denotes formally all corrections of relativistic origin, which involves at least one power of the fine-structure constant α. The calculated spin-orbit splitting is given by the differ-

TABLE I. Spin-orbit splitting (in cm^{-1}) in the ground states of B- and F-like ions.

	B Sequence: $(2p)\,^2P_{1/2} - (2p)\,^2P_{3/2}$					F Sequence: $(2p^5)\,^2P_{1/2} - (2p^5)\,^2P_{3/2}$		
		MC				SC		
Ion	SC[a]	Previous[b]	Corrected[c]	Experiment[d]	Ion	Previous[b]	Corrected[c]	Experiment[d]
B	15.7	435.3	15.7	16[e]	F	375.2	399.0	404.1
C^+	64.4	271.5	62.7	63.42[f]	Ne^+	755.7	774.3	780.34
N^{2+}	179	335.8	172.4	174.5[e]	Na^{2+}	1343	1359	1366.4
Ne^{5+}	1346	1472	1298	1310	Mg^{3+}	2206	2221	2228
Na^{6+}	2199	2308	2124	2139[g]	Si^{5+}	5071	5084	5100
Si^{9+}	7194	7183	6968	6990	Cl^{8+}	13 624	13 636	13 600
Ar^{13+}	23 286	22 856	22 612	22 655.9	Ca^{11+}	30 044	30 055	30 044[k]
V^{18+}		68 808	68 539	68 610[h]	Ti^{13+}	47 218	47 229	47 219[l]
Cr^{19+}		83 131	82 857	82 926[i]	Cr^{15+}	70 908	70 919	70 892[l]
Fe^{21+}	121 142	118 458	118 177	118 266[i]	Fe^{17+}	102 618	102 629	102 580[l]
Ni^{23+}		164 176	163 889	164 000[j]	Ni^{19+}	144 027	144 038	143 978[l]
Zn^{25+}		222 255	221 963		Zn^{21+}	196 995	197 006	
Kr^{31+}		492 881	492 576		Kr^{27+}	446 772	446 783	
Mo^{37+}		964 666	964 352		Mo^{33+}	886 993	887 003	

[a] Present single-configuration results.
[b] Multiconfiguration results in Ref. 3.
[c] Present multiconfiguration results.
[d] Cited in Ref. 6, unless specified otherwise.
[e] Cited in Ref. 7.
[f] Ref. 8.
[g] Ref. 9.
[h] Ref. 10.
[i] Ref. 11.
[j] Ref. 12.
[k] Ref. 13.
[l] Ref. 14.

ence of $E(^2P_{1/2})$ and $E(^2P_{3/2})$,

$$\omega_{\text{calc.}} = E(^2P_{1/2}) - E(^2P_{3/2}) = [u_{1/2}(Z) - u_{3/2}(Z)] + \alpha[v_{1/2}(Z,\alpha) - v_{3/2}(Z,\alpha)]. \quad (5)$$

Because the spin-orbit splitting is purely of relativistic origin, the "true" spin-orbit splitting must involve at least one power of α:

$$\omega_{\text{true}} = \alpha v(Z,\alpha). \quad (6)$$

Thus, in calculating ω, care should be taken to ensure that the nonrelativistic energy term, $\Delta u = u_{1/2}(Z) - u_{3/2}(Z)$, is zero to avoid erroneous contributions to the spin-oribt splitting.

Obviously, inconsistent choices of configurations in relativistic SCF calculations can lead to different nonrelativistic correlation energies for the $^2P_{1/2}$ and $^2P_{3/2}$ states, and hence to nonvanishing values of Δu. There is, however, another mechanism characteristic of the relativistic SCF procedure that introduces nonzero Δu terms even in single-configuration calculations. Relativistically, two orbitals with the same n,l but different j quantum numbers, such as $2p_{3/2}$ and $2p_{1/2}$, have different radial functions. Nevertheless they are expected to converge to the same nonrelativistic limit, when the fine-structure constant is set equal to zero. In the relativistic SCF procedure, however, as was pointed out by Wood and Pyper,[15] when a configuration has more than one parent core state—such as the $(2p^4)\,^3P$, ^1D, and ^1S core states of the F-like ions—the two radial functions $2p_{3/2}$ and $2p_{1/2}$ do not converge to the same nonrelativistic limit unless they are forced to do so through additional constraints. When the core states are not unique, a singly excited configuration, such as $2p^43p$, can interact[16] with the ground-state configuration $2p^5$. The resulting $2p_{3/2}$ and $2p_{1/2}$ radial functions are thus mixed with the $3p$ radial function through variational calculations and eventually converge to different nonrelativistic limits. In the multiconfiguration calculations of B-like ions, because we include all $2p^3$ relativistic configurations which have three parent core states $(2p^2)\,^3P$, ^1D, and ^1S, a similar situation to the F-like ions also exists. These spurious nonrelativistic contributions, Δu, should be removed from theoretical spin-orbit splittings before comparisons are made with experiment. They can easily be calculated by setting the fine-structure constant equal to zero in the Dirac-Fock program.[4]

The corrected Dirac-Fock results for B- and F-like ions are also given in Table I. This correction dramatically improves the multiconfiguration results of B-like ions and brings them into harmony with experiment. On the other hand, we note that the single-configuration calculations for the $(2s^22p)\,^2P_{1/2}$ and the $(2s^22p)\,^2P_{3/2}$ levels of B-like ions have a common, unique parent state, $(2s^2)\,^1S$, such that $\Delta u = 0$ and no correction is needed. Nevertheless, the corrected multiconfiguration results provide a slightly better agreement with experiment. For F-like ions, we can also see that the corrected results agree better with experiment for ions of low ionicity.

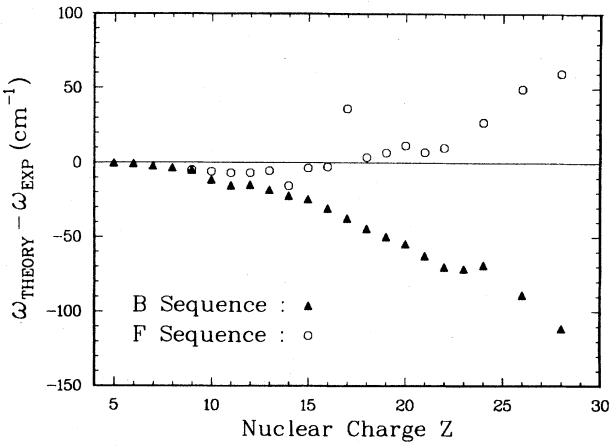

FIG. 1. Comparison between theory and experiment of the spin-orbit splitting, $^2P_{1/2}$-$^2P_{3/2}$, in the ground states of B- and F-like ions.

In Fig. 1, we plot the difference, $\Delta\omega$, between the theory and experiment as a function of the nuclear charge Z. Based on the Z dependence of $\Delta\omega$ a critical judgement of the reliability of available experimental data is possible. Furthermore, by extrapolation of the smooth Z dependence of $\Delta\omega$ we can make a semiempirical correction on theoretical calculations and predict the spin-orbit splitting in heavy ions with high precision unattainable with *ab initio* calculations alone.

In conclusion, we emphasize that theoretical transition energies obtained through separate initial- and final-state calculations can suffer from the inherent difficulty of treating the two states in a balanced manner. For fine structures of light atoms, molecules, or ions, this difficulty becomes even more serious because the error introduced is a substantial fraction of the actual level splitting. As demonstrated by the examples given in Tables I, the present method of eliminating spurious level separations provides an easy remedy for spin-orbit splitting cal-

culations involving the relativistic SCF procedure. A judicious use of the theoretical method described here in combination with experimental data will allow us not only to identify any irregularity in the experimental data, but also to make reliable semiempirical predictions. Additional work is in progress on a number of forbidden transitions among the fine-structure levels for ions of interest to astrophysics and plasma diagnostics.

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