by mixing into it all the configurations of two particles and two holes (the one-particle one-hole configurations are not coupled to the SCF ground state by construction). We have then calculated the occupation numbers in the perturbed ground state and found that the occupancy of particle states just above the Fermi level and of hole states just below it is of the order of a few percent. This result suggests that the system of π electrons may be treated within the framework of the random-phase approximation.

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Calculated Wavelengths for Transitions Between S and P States in Two-Electron Atoms and Comparison with Experiment

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Theoretical wavelengths are calculated for the 2^1S-2^1P and the 3^3P-4^3S transitions in C v, and for the 2^3S-3^3P, 2^3S-4^3P and 2^3S-5^3P transitions in C v, N vi, and O vii. The theoretical wavelengths are compared with the results of recent measurements using laser-produced plasmas. When the mass-polarization and relativistic effects are included, the calculations agree with the experimental results in most cases, and thus assist in verifying the identification of some new spectral lines.

INTRODUCTION

Recent experimental work[1,2] on laser-produced plasmas has resulted in the appearance of many new spectral lines, not all of which can easily be identified. It is desirable, therefore, to have theoretical results available for the purpose of line prediction and identification, both for these and for future experiments. Many of the lines observed belong to transitions between S and P

states of two-electron atoms, and we are at present engaged on a program to calculate term values for the low-lying S and P states of the helium isoelectronic sequence up to $Z=10$. In the present work, we give theoretical values for the wavelengths of transitions which have recently been observed in the two-electron atoms C v, N vi, and O vii. In most cases the theoretical values agree with the experimental results to well within the accuracy of the latter.

CALCULATIONS AND RESULTS

The methods used to obtain theoretical term values have been described in detail previously.[3–5] The nonrelativistic Schrödinger wave equation for a two-electron atom with an assumed infinitely heavy nucleus is solved by an expansion of the form $e^{-\xi r_1 - \eta r_2}$ times a triple series in r_1, r_2, and r_3, the distances of the two electrons from the nucleus and from one another. (In view of the triangle condition on r_1, r_2, and r_3, a transformation is first made to "perimetric coordinates," linear combinations of these coordinates which range from zero to infinity.) From the eigenvalue E of the Schrödinger equation for the state in question, we obtain the nonrelativistic ionization potential J_{nr} from the relation $J_{\mathrm{nr}} = -(2E+Z^2)R_M$. The finite mass of the nucleus is taken into account by the use of the appropriate reduced Rydberg constant R_M, and by the addition of the "mass-polarization correction" $-\epsilon_M$ to the ionization potential. Relativistic effects to order α^2 are taken into account by the addition of the relativistic corrections,[5] denoted by E_J, so that the final theoretical ionization potential J_{th} is given by $J_{\mathrm{th}} = J_{\mathrm{nr}} + E_J - \epsilon_M$. No Lamb-shift correction is applied.

In Table I we give the values of J_{nr}, $E_J - \epsilon_M$, and J_{th} for the states 2^1S, 2^3S, 4^3S, 2^1P, 3^3P, 4^3P, and 5^3P of C v, and for the 2^3S, 3^3P, 4^3P, and 5^3P states of N vi and O vii. The value of J_{nr} for the 2^1S state of C v was obtained using expansions containing up to 1078 terms, with the nonlinear parameters ξ and η being assigned the value $(-E)^{1/2}$ (method B).[3] In the case of the remaining S states, the asymmetric values of $\xi=(-2E-Z^2)^{1/2}$, $\eta=Z$, were adopted, with an expansion of 220 terms, and the image function was added in which the two electrons were permuted (method C).[4] For all of the S states, the values of $E_J - \epsilon_M$ were obtained to more than sufficient accuracy using type C expansions containing 120 terms. In the case of the P states, we set η equal to Z, while ξ was optimized so as to obtain the best possible value for the energy, for a given number of terms in the expansion (method D).[5] The values of J_{nr} were obtained using expansions containing up to 364 terms, while the values of $E_J - \epsilon_M$ were obtained from expansions containing 120 terms.

TABLE I. Theoretical ionization energies. J_{nr} denotes the nonrelativistic ionization energy, $E_J - \epsilon_M$ the relativistic and mass-polarization corrections, and $J_{\mathrm{th}} = J_{\mathrm{nr}} + E_J - \epsilon_M$ the total theoretical ionization energy.

State		J_{nr} (cm^{-1})	$E_J-\epsilon_M$ (cm^{-1})	J_{th} (cm^{-1})
C v	2^1S	707 119	268	707 387
	2^3S	750 735	414	751 149
	4^3S	178 808	60	178 868
	2^1P	678 877	147	679 024
	3^3P	310 923	75	310 998
	4^3P	174 006	35	174 041
	5^3P	111 030	19	111 049
N vi	2^3S	1 066 096	811	1 066 907
	3^3P	446 517	156	446 673
	4^3P	250 060	73	250 133
	5^3P	159 624	40	159 664
O vii	2^3S	1 436 335	1440	1 437 775
	3^3P	606 503	290	606 793
	4^3P	339 834	136	339 970
	5^3P	216 998	74	217 072

COMPARISON WITH EXPERIMENT

In Table II, we compare the theoretical and experimental values for the wavelengths of the 2^1S-2^1P and 3^3P-4^3S transitions in C v and the 2^3S-3^3P, 2^3S-4^3P, and 2^3S-5^3P transitions in C v, N vi, and O vii. The wave number ν_{nr} is equal to the difference in the values of the nonrelativistic ionization potentials J_{nr} for the two states in question, while the wave number ν_{th} is the difference of the two corresponding values of J_{th}, and therefore includes the contributions from the mass-polarization and relativistic corrections. λ_{nr} and λ_{th} are the wavelengths corresponding to ν_{nr} and ν_{th}, respectively, while λ_{expt} denotes the experimentally determined wavelength for the transition.

It will be seen that when the relativistic and mass-polarization corrections are taken into account, the theoretical values for the wavelength of the transition agree with the experimental values to within the estimated accuracy of the latter, except in the case of the 2^1S-2^1P and 3^3P-4^3S transitions in C v, and the 2^3S-4^3P transition in O vii. In the first and third cases, the discrepancy between theory and experiment is no more than twice the estimated uncertainty of the latter. For the 2^1S-2^1P transition in C v, the difference in $\lambda_{\mathrm{expt}} - \lambda_{\mathrm{th}}$ is 1.0 ± 0.5 Å in the wavelength, corresponding to -8 ± 4 cm^{-1} in the wave number, a comparatively small difference in energy.[6] The large discrepancy in the case of the 3^3P-4^3S transition in C v would tend to show that

TABLE II. Theoretical and experimental wave numbers and wavelengths. ν_{nr} and λ_{nr} denote the nonrelativisitic values of the wave number and wavelength of the transition, ν_{th} and λ_{th} denote the corresponding values after inclusion of the mass-polarization and relativistic corrections, and λ_{expt} denotes the experimentally measured wavelength.

Transition		ν_{nr} (cm^{-1})	ν_{th} (cm^{-1})	λ_{nr} (Å)	λ_{th} (Å)	λ_{expt} (Å)	Ref.
C v	2^1S–2^1P	28 242	28 363	3540.8	3525.7	3526.7 ± 0.5	1
	2^3S–3^3P	439 812	440 151	227.37	227.19	227.22 ± 0.04	2
	2^3S–4^3P	576 729	577 108	173.39	173.28	173.27 ± 0.04	2
	2^3S–5^3P	639 705	640 100	156.32	156.23	156.23 ± 0.04	2
	3^3P–4^3S	132 115	132 130	756.9	756.8	765.4 ± 0.2	1
N vi	2^3S–3^3P	619 579	620 234	161.40	161.23	161.22 ± 0.04	2
	2^3S–4^3P	816 036	816 774	122.54	122.43	122.44 ± 0.04	2
	2^3S–5^3P	906 472	907 243	110.32	110.22	110.23 ± 0.04	2
O vii	2^3S–3^3P	829 832	830 982	120.51	120.34	120.37 ± 0.05	8
	2^3S–4^3P	1 096 501	1 097 805	91.20	91.09	91.02 ± 0.05	8
	2^3S–5^3P	1 219 337	1 220 703	82.01	81.92	81.89 ± 0.05	8

the line at 765.4 Å, tentatively identified[1] as belonging to this transition, in fact arises from some other transition.[7]

CONCLUSIONS

The results shown in Table II indicate that in most cases, the accuracy of the experimentally determined wavelength for a given transition may be matched by the difference between the computed term values for the two states, if and only if the mass-polarization and α^2 relativistic corrections are taken into account. For transitions between close-lying states, however, the Lamb-shift correction may well have to be included in order to achieve the experimental accuracy. The theoretical values are thus able to be of considerable use, both as an aid in the identification of new spectral lines, and also in predicting the location of the line corresponding to a given transition.

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