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S and *P* States of the Helium Isoelectronic Sequence up to $Z = 10$

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Calculations have been made of the energy levels and other properties of the states $n\,^1S$, $n\,^3S$, $n\,^1P$, and $n\,^3P$, $n=2$ to 5, for atoms belonging to the helium isoelectronic sequence up to $Z=10$, and also for the higher excited *S* states of helium. The theoretical term values, including the contributions from the mass-polarization correction and the relativistic effects of order α^2 are listed. A detailed comparison with the experimentally determined energy differences between *S* and *P* states for He I up to F VIII shows a satisfactory agreement in almost every case, provided that we include an estimate of the Lamb-shift correction to the *S*-state energy level when considering transitions involving the $1\,^1S$, $2\,^1S$, or $2\,^3S$ states.

I. INTRODUCTION

In this paper, we shall present the results of a systematic calculation of the energy levels and other properties of the low-lying *S* and *P* states for two-electron atoms up to $Z=10$. We have also calculated *f* values for transitions between these states, and the results will be presented in a forthcoming paper.[1]

On the experimental side, high-precision measurements of the energy difference between *S* and *P* levels in two-electron atoms were made as long as three decades ago.[2–4] Since that time, the accuracy of the experiments has been further improved, and many more lines have been measured.[5–12] Laser-produced plasmas have recently proved to be a fruitful source of heliumlike ions.[13–14] The advent of extraterrestrial spectroscopy has also led to quite a number of observations of two-electron spectra,[15–18] and the accuracy of measurements from this source will no doubt improve in the future. The observations on two-electron spectra now extend from the infrared to the x-ray region around 15 Å.

The method used in our calculations is basically the same as that employed for helium, the wavefunction being expanded in a triple series of Laguerre polynomials of the *perimetric* coordinates.[19–24] The expansion includes the interelectronic distance explicitly, and is thus particularly appropriate for the low-lying states, where the correlation effects are important. The effectiveness of the method decreases as the order of the excited state is increased. We have therefore carried out the calculation by this method for the 16 lowest excited states $n\,^1S$, $n\,^3S$, $n\,^1P$, and $n\,^3P$, $n=2, 3, 4, 5$. In the case of He, we have carried our calculation up to the $15\,^1S$ and $17\,^3S$ states, which cover all of the observations.[25] However, the determination of the higher excited states by the present method necessitates the use of very large expansions (containing up to about 2000 terms), and these calculations were therefore not repeated for other atoms. The results presented here, and in a paper in preparation, represent therefore the maximum which we think could be achieved by the present method using the current generation of computers.

In Sec. II, we describe the method used in the calculations, and the numerical results obtained are listed in Tables III–XXII of Sec. III. In Sec. IV, we list our final theoretical term values and compare the results with experiment. Our comparison underlines the need for a calculation of the

TABLE I. Convergence of the nonrelativistic ionization energy J_{nr} as the number of terms in the expansion is increased. $J_{nr}(C)$ and $J_{nr}(D)$ are the values obtained using type-C and -D expansions, respectively, and ξ_{opt} is the optimum value of ξ for the type-D expansion.

State		He			Cv			Ne IX		
		$J_{nr}(C)$ (cm^{-1})	$J_{nr}(D)$ (cm^{-1})	ξ_{opt}	$J_{nr}(C)$ (cm^{-1})	$J_{nr}(D)$ (cm^{-1})	ξ_{opt}	$J_{nr}(C)$ (cm^{-1})	$J_{nr}(D)$ (cm^{-1})	ξ_{opt}
$2\,^1S$ order	20	31 922.17	31 975.15	0.69152	706 978.76	707 027.52	2.91715	2 259 358.59	2 259 400.76	5.07182
	56	32 012.20	32 029.18	0.81157	707 100.18	707 113.41	3.43217	2 259 485.31	2 259 497.67	5.94323
	120	32 028.44	32 032.83	0.92911	707 115.32			2 259 500.44		
	220	32 031.91			707 117.95			2 259 503.02		
$2\,^3S$ order	20	38 452.61	38 452.74	0.65307	750 734.03	750 734.12	2.76351	2 341 432.08	2 341 432.17	4.82324
	56	38 453.03	38 453.09	0.77430	750 734.69	750 734.73	3.15274	2 341 432.80	2 341 432.83	5.44366
	120	38 453.11	38 453.13	0.88498	750 734.75			2 341 432.86		
	220	38 453.12								
$5\,^1S$ order	56	4 621.58	4 623.65	0.21549	111 064.74	111 066.14	1.02665	358 007.71	358 008.72	1.83118
	120	4 635.35	4 640.44	0.25789	111 090.34	111 097.13	1.17865	358 035.46	358 042.05	2.07152
	220	4 641.32	4 645.54	0.29582	111 099.76	111 104.50	1.32529	358 045.44	358 050.06	2.31899
	364	4 644.17			111 103.53			358 049.33		
$5\,^3S$ order	56	4 952.48	4 956.12	0.22558	113 440.98	113 441.81	1.03125	362 450.73	362 451.17	1.83195
	120	4 962.61	4 963.36	0.24793	113 446.67	113 446.73	1.09649	362 455.52	362 455.55	1.93817
	220	4 963.50	4 963.58	0.26555	113 446.76	113 446.77	1.24111	362 455.58	362 455.60	2.17933
	364	4 963.58			113 446.77			362 455.60		

Lamb-shift correction, at least for the $2\,^1S$ and $2\,^3S$ states. If even a rough order-of-magnitude estimate for this correction is included, the agreement between theory and experiment is found to be satisfactory in almost every case.

II. COMPUTATIONAL METHOD

The methods used to compute theoretical values for the ionization potential of an S or P state of a two-electron atom or ion have been described in detail in previous publications.[19–24,26] It will, therefore, suffice to give here only a brief description of the main steps involved.

The Schrödinger wave equation for a two-electron atom with an infinitely heavy nucleus

$$\nabla_1^2\psi+\nabla_2^2\psi+2[E+(Z/r_1)+(Z/r_2)-(1/r_3)]\psi=0 \quad (1)$$

is first solved to obtain the so-called "nonrelativistic energy" E and the corresponding wave function ψ for the given state. In this equation, ∇_1^2 and ∇_2^2 denote the Laplacian with respect to the coordinates of electron 1 and electron 2; r_1 and r_2 are the distances of the two electrons from the nucleus; and r_3 denotes the interelectronic distance. The energy E is given in a.u. Relativistic effects, up to order α^2, are taken into account by computing the so-called "relativistic corrections," which take the form of the expectation values of various operators evaluated over the nonrelativistic wave function ψ. Corrections are made for the finite mass of the nucleus by using an appropriate value R_M for the Rydberg constant, when converting the energy from a. u. into cm^{-1}, and by the addition of the so-called "mass-polarization correction," which again takes the form of the expectation value of a certain operator evaluated over ψ.

The solution of Eq. (1) is obtained by solving an equivalent variational problem, the variation integral being taken over the six-dimensional coordinate space of the two electrons. Since the Hamiltonian is invariant with respect to rotation about any axis through the nucleus, the angular dependence of the wave functions may be determined *a priori*, and integration over these coordinates carried out immediately. The dependence of the wave function on the three coordinates r_1, r_2, and r_3 remains to be determined. These three variables have to satisfy the triangle condition, and in order to avoid the resulting inconvenient limits of integration, a transformation is made to the "perimetric coordinates" u, v, and w which are linear combinations[19,23] of r_1, r_2, and r_3, so chosen as to all range from zero to infinity. In terms of these coordinates, the wave function is assumed to be of the form

$$\psi=(1\pm P_{12})e^{-(u+v+w)/2}F(u,\,v,\,w)\ , \quad (2)$$

where for the case of the S states the expansion

TABLE II. Convergence of the nonrelativistic ionization energy J_{nr} for P states as the number of terms in the expansion is increased (method D).

		He		C V		Ne IX	
State		ξ	J_{nr} (cm^{-1})	ξ	J_{nr} (cm^{-1})	ξ	J_{nr} (cm^{-1})
$2\,^1P$ order	20	0.696	27 166.016	3.116	678 857.544	5.442	2 206 882.376
	56	0.77	27 176.090	3.434	678 876.161	6.008	2 206 904.397
	120	0.834	27 176.640	3.752	678 876.833	6.572	2 206 905.178
	220	0.90	27 176.683	4.064	678 876.878	7.124	2 206 905.230
	364	0.96	27 176.688	4.36	678 876.882	7.65	2 206 905.235
$2\,^3P$ order	20	0.725[a]	29 210.757	3.070	707 045.136	5.314	2 264 358.523
	56	0.7914[a]	29 221.792	3.411	707 051.171	5.924	2 264 364.532
	120	0.845[a]	29 222.133	3.732	707 051.376	6.478	2 264 364.749
	220	0.91[a]	29 222.152	4.034	707 051.390	7.014	2 264 364.763
	364	0.98[a]	29 222.154	4.32	707 051.391	7.54	2 264 364.765
$5\,^1P$ order	20	0.197	4 348.047	0.994	109 282.321	1.794	354 699.531
	56	0.221	4 355.840	1.084	109 320.613	1.927	354 746.771
	120	0.260	4 364.002	1.24	109 353.455	2.182	354 786.248
	220	0.295	4 367.208	1.37	109 361.184	2.406	354 795.188
	364	0.33	4 368.020	1.49	109 362.378	2.62	354 796.508
	560	0.36	4 368.202	1.60	109 362.554	2.80	354 796.697
$5\,^3P$ order	20	0.206	4 473.342	1.016	110 934.774	1.818	357 980.567
	56	0.241	4 493.186	1.132	111 004.909	1.991	358 059.648
	120	0.280	4 505.607	1.263	111 026.460	2.207	358 082.758
	220	0.309	4 509.011	1.373	111 029.548	2.395	358 085.875
	364	0.34	4 509.695	1.47	111 029.868	2.55	358 086.176
	560	0.37	4 509.811	1.57	111 029.902	2.70	358 086.208

[a] See Ref. 27.

$$F=\sum_{l,m,n} P(l,\,m,\,n)L_l(u)L_m(v)\,L_n(w) \tag{3}$$

is assumed, and for the P states,

$$F=r_1\cos\theta_1\sum_{l,m,n} Q(l,\,m,\,n)u^l v^m w^n\,, \tag{4}$$

where θ_1 is the polar angle of electron 1. The use of Laguerre polynomials in (3) is advantageous because of their orthogonality properties. However, they were not used in the case of the P states because of the complexity of the resulting equations. Substitution of the form (2) into the variational integral and application of the variation conditions leads to a homogeneous set of simultaneous linear equations for the coefficients $P(l,\,m,\,n)$ or $Q(l,\,m,\,n)$, and the requirement that the determinant of coefficients should vanish yields eigenvalues for the energy E. Each eigenvalue corresponds to a state of the given symmetry, and the corresponding vector of coefficients $P(l,\,m,\,n)$ or $Q(l,\,m,\,n)$ gives a representation of the wave function for this state.

In the actual computation, truncated expansions containing all terms for which the sum $(l+m+n)$ is less than a given number Ω were used; the convergence of the eigenvalue as Ω is increased giving an indication of the accuracy achieved. In most cases, we used the values $\Omega=3$, 5, 7, 9, and 11, corresponding to expansions containing 20, 56, 120, 220, and 364 terms, respectively. The maximum Ω used was 22, corresponding to 2300 terms.

The exponential factor in (2) is of the form $e^{-\xi r_1-\eta r_2}$. In the earlier method, which we call method C,[23] η was taken to be equal to the atomic number Z, while ξ was given the value $(-2E-Z^2)^{1/2}$. These values give the correct asymptotic behavior as one or other of the electrons goes to infinity. It was found, however, that the convergence was improved considerably if the parameter ξ was also allowed to vary, and its value chosen so as to make the energy E a minimum for a given number of terms in the expansion. We shall refer to this scheme as method D.[24] For the $2\,^1S$ state, computations were also carried out using method B,[22] in which the expansion is of the form

$$\psi=e^{-(u+v+w)/2}\sum_{l,m,n} B(l,\,m,\,n)L_l(u)L_m(v)L_n(w), \tag{5}$$

where the exponential factor has $\xi=\eta=(-E)^{1/2}$. Because of the greater symmetry of this wave function, the matrix whose determinant has to be evaluated has a much greater proportion of zero elements than in cases of methods C and D, thus enabling expansions containing a much larger number of terms to be used. However, this method was found[23] to yield poor results for the higher excited

TABLE III. Ionization energy and the expectation values of various operators for the low-lying excited S states of He. J_{nr} denotes the nonrelativistic ionization energy, and $J_{theor} = J_{nr} + E_J - \epsilon_M$ is the total theoretical ionization energy (excluding the Lamb-shift correction).

State	$2\,^1S$	$3\,^1S$	$4\,^1S$	$5\,^1S$	$2\,^3S$	$3\,^3S$	$4\,^3S$	$5\,^3S$
$J_{nr}(\text{cm}^{-1})$	32 033.206	13 445.8	7 370.4	4 647.1	38 453.12925	15 073.439	8 012.377	4 963.59
$E_J(\text{cm}^{-1})$	0.400	0.140	0.064	0.034	1.9220	0.5269	0.2137	0.1068
$-\epsilon_M(\text{cm}^{-1})$	−0.28591	−0.080	−0.033	−0.02	−0.22388810	−0.0571	−0.02237	−0.01096
$J_{theor}(\text{cm}^{-1})$	32 033.321	13 445.8	7 370.4	4 647.1	38 454.8274	15 073.909	8 012.568	4 963.68
$\langle\delta(\vec{r}_1)\rangle$ (a.u.)	1.30945	1.28312	1.2772	1.2752	1.320355	1.285060	1.277853	1.275496
$\langle\delta(\vec{r}_3)\rangle$ (a.u.)	0.00865	0.0025	0.001	0.001	0	0	0	0
$\langle r_1\rangle$ (a.u.)	2.97306	6.512	11.55	18.10	2.5504627	5.85598	10.6612	16.96637
$\langle r_1^2\rangle$ (a.u.)	16.0891	85.9	281.5	704	11.46432	68.709	238.580	617.179
$\langle r_3\rangle$ (a.u.)	5.26969	12.305	22.37	35.5	4.447535	10.9988	20.5917	33.19455
$\langle r_3^2\rangle$ (a.u.)	32.302	171.9	563	1 408	23.04620	137.475	477.194	1 234.380

TABLE IV. Ionization energy and the expectation values of various operators for the low-lying excited S states of Li II.

State	$2\,^1S$	$3\,^1S$	$4\,^1S$	$5\,^1S$	$2\,^3S$	$3\,^3S$	$4\,^3S$	$5\,^3S$
$J_{nr}(\text{cm}^{-1})$	118 699.433	51 299.4	28 481.9	18 089.3	134 028.674	55 320.056	30 095.65	18 893.7
$E_J(\text{cm}^{-1})$	6.515	2.336	1.07	0.57	16.8870	5.120	2.176	1.118
$-\epsilon_M(\text{cm}^{-1})$	−0.372515	−0.109	−0.046	−0.02	−0.301523	−0.08282	−0.0336	−0.01680
$J_{theor}(\text{cm}^{-1})$	118 705.575	51 301.6	28 482.9	18 089.8	134 045.260	55 325.094	30 097.79	18 894.8
$\langle\delta(\vec{r}_1)\rangle$ (a.u.)	4.5188	4.3600	4.3231	4.310	4.56379	4.36886	4.32607	4.31158
$\langle\delta(\vec{r}_3)\rangle$ (a.u.)	0.065	0.019	0.008	0.004	0	0	0	0
$\langle r_1\rangle$ (a.u.)	1.64421	3.4618	6.031	9.35	1.4938934	3.234999	5.7261	8.967108
$\langle r_1^2\rangle$ (a.u.)	4.6951	23.600	75.37	185.7	3.773591	20.40329	67.634	170.3757
$\langle r_3\rangle$ (a.u.)	2.84445	6.4488	11.576	18.21	2.561469	5.999510	10.9680	17.44411
$\langle r_3^2\rangle$ (a.u.)	9.4371	47.22	150.8	371.5	7.583692	40.82670	135.280	340.7595

TABLE V. Ionization energy and the expectation values of various operators for the low-lying excited S states of Be III.

State	$2\,^1S$	$3\,^1S$	$4\,^1S$	$5\,^1S$	$2\,^3S$	$3\,^3S$	$4\,^3S$	$5\,^3S$
J_{nr} (cm^{-1})	260 033.913	113 529	63 313^a	40 313^a	284 677.8	120 039.18	65 938.34(+2)	41 626.27
E_J (cm^{-1})	33.8	12.20	5.6	2.99	66.88	21.192	9.19	4.78
$-\epsilon_M$ (cm^{-1})	−0.455	−0.137	−0.06	−0.03	−0.3758	−0.10624	−0.044	−0.0220
$J_{\rm theor}$(cm^{-1})	260 067.3	113 541	63 319^a	40 316^a	284 744.3	120 060.26	65 947.49(+2)	41 631.02
$\langle\delta(\vec{r}_1)\rangle$ (a.u.)	10.8611	10.3800	10.267	10.2269	10.9629	10.40079	10.2737	10.23001
$\langle\delta(\vec{r}_3)\rangle$ (a.u.)	0.215	0.064	0.03	0.01	0	0	0	0
$\langle r_1\rangle$ (a.u.)	1.13977	2.3630	4.0875	6.312	1.063671	2.249723	3.93577	6.12182
$\langle r_1^2\rangle$ (a.u.)	2.2078	10.848	34.32	84.1	1.88178	9.749735	31.6994	78.9709
$\langle r_3\rangle$ (a.u.)	1.94804	4.3713	7.812	12.257	1.810526	4.148298	7.50949	11.87677
$\langle r_3^2\rangle$ (a.u.)	4.4376	21.706	68.65	168.3	3.77914	19.50848	63.404	157.9455

[a] Denotes an extrapolated value.

TABLE VI. Ionization energy and the expectation values of various operators for the low-lying excited S states of B IV.

State	$2\,^1S$	$3\,^1S$	$4\,^1S$	$5\,^1S$	$2\,^3S$	$3\,^3S$	$4\,^3S$	$5\,^3S$
J_{nr} (cm^{-1})	456 161.411	200 150	111 866	71 319^a	490 259.3	209 171.76	115 511.84(+2)	73 145.52
E_J (cm^{-1})	108.7	39.30	18.0	10	184.87	60.050	26.34	13.78
$-\epsilon_M$ (cm^{-1})	−0.506	−0.155	−0.067	−0.04	−0.4248	−0.12192	−0.0505	−0.0256
$J_{\rm theor}$ (cm^{-1})	456 269.6	200 189	111 884	71 329^a	490 443.8	209 231.69	115 538.13(+2)	73 159.27
$\langle\delta(\vec{r}_1)\rangle$ (a.u.)	21.4109	20.3335	20.078	19.988	21.5920	20.37115	20.0906	19.9933
$\langle\delta(\vec{r}_3)\rangle$ (a.u.)	0.51	0.149	0.06	0.03	0	0	0	0
$\langle r_1\rangle$ (a.u.)	0.87293	1.79491	3.0927	4.766	0.8271511	1.7272760	3.002408	4.652544
$\langle r_1^2\rangle$ (a.u.)	1.27879	6.2082	19.549	47.79	1.127878	5.708315	18.3627	45.46655
$\langle r_3\rangle$ (a.u.)	1.48104	3.3065	5.895	9.238	1.402139	3.1743611	5.71564	9.011901
$\langle r_3^2\rangle$ (a.u.)	2.5696	12.4221	39.101	95.59	2.26377	11.421396	36.7283	90.93509

[a] Denotes an extrapolated value.

TABLE VII. Ionization energy and the expectation values of various operators for the low-lying excited S states of C V.

State	$2\,^1S$	$3\,^1S$	$4\,^1S$	$5\,^1S$	$2\,^3S$	$3\,^3S$	$4\,^3S$	$5\,^3S$
J_{nr} (cm^{-1})	707 118.767	311 158	174 139[a]	111 106[a]	750 734.75	322 701.38	178 807.91(+2)	113 446.77
E_J (cm^{-1})	268.6	97.06	44.48	24	414.7	136.90	60.50	31.78
$-\epsilon_M$ (cm^{-1})	−0.587	−0.181	−0.08	−0.04	−0.4980	−0.14427	−0.0600	−0.0305
J_{theor} (cm^{-1})	707 386.8	311 255	174 183[a]	111 130[a]	751 149.0	322 838.13	178 868.35(+3)	113 478.52
$\langle\delta(\vec{r}_1)\rangle$ (a.u.)	37.2425	35.2110	34.726	34.555	37.5252	35.2702	34.7465	34.5642
$\langle\delta(\vec{r}_3)\rangle$ (a.u.)	0.99	0.29	0.12	0.06	0	0	0	0
$\langle r_1\rangle$ (a.u.)	0.707576	1.44742	2.4879	3.829	0.6770597	1.4025630	2.42808	3.753592
$\langle r_1^2\rangle$ (a.u.)	0.83330	4.01553	12.607	30.770	0.751498	3.747393	11.9735	29.53196
$\langle r_3\rangle$ (a.u.)	1.19456	2.65905	4.7340	7.412	1.1446656	2.5720177	4.61542	7.26303
$\langle r_3^2\rangle$ (a.u.)	1.67388	8.0345	25.216	61.54	1.50764	7.497601	23.9488	59.06511

[a] Denotes an extrapolated value.

TABLE VIII. Ionization energy and the expectation values of various operators for the low-lying excited S states of N VI.

State	$2\,^1S$	$3\,^1S$	$4\,^1S$	$5\,^1S$	$2\,^3S$	$3\,^3S$	$4\,^3S$	$5\,^3S$
J_{nr} (cm^{-1})	1 012 926.91	446 556	250 131[a]	159 673[a]	1 066 096.06	460 624.53	255 825.0	162 529.22
E_J (cm^{-1})	562.0	202.85	92.9	50	811.4	270.83	120.3	63.38
$-\epsilon_M$ (cm^{-1})	−0.608	−0.190	−0.08	−0.04	−0.5199	−0.15157	−0.063	−0.0322
J_{theor} (cm^{-1})	1 013 488.3	446 759	250 224[a]	159 723[a]	1 066 906.9	460 895.21	255 945.2	162 592.56
$\langle\delta(\vec{r}_1)\rangle$ (a.u.)	59.4303	56.0026	55.182	54.891	59.837	56.0883	55.2114	54.9050
$\langle\delta(\vec{r}_3)\rangle$ (a.u.)	1.70	0.50	0.21	0.11	0	0	0	0
$\langle r_1\rangle$ (a.u.)	0.594992	1.21283	2.0811	3.1996	0.5732130	1.1809225	2.038641	3.146364
$\langle r_1^2\rangle$ (a.u.)	0.585803	2.80862	8.8000	21.455	0.5365973	2.6485039	8.42299	20.71914
$\langle r_3\rangle$ (a.u.)	1.000916	2.22370	3.9552	6.190	0.9672979	2.1622649	3.371087	6.083557
$\langle r_3^2\rangle$ (a.u.)	1.17632	5.6194	17.601	42.911	1.076121	5.2988061	16.84711	41.43903

[a] Denotes an extrapolated value.

TABLE IX. Ionization energy and the expectation values of various operators for the low-lying excited S states of O VII.

State	$2\,^1S$	$3\,^1S$	$4\,^1S$	$5\,^1S$	$2\,^3S$	$3\,^3S$	$4\,^3S$	$5\,^3S$
J_{nr} (cm^{-1})	1 373 591.24	606 342	339 842^{a}	217 020^{a}	1 436 334.68	622 937.52	346 561.1	220 391.73
E_J (cm^{-1})	1 048	377.9	173.1	93	1 440.6	484.85	216.2	114.14
$-\epsilon_M$ (cm^{-1})	−0.624	−0.196	−0.09	−0.05	−0.5369	−0.15724	−0.0658	−0.0335
J_{theor} (cm^{-1})	1 374 639	606 720	340 015^{a}	217 113^{a}	1 437 774.7	623 422.21	346 777.2	220 505.84
$\langle\delta(\vec{r}_1)\rangle$ (a.u.)	89.0485	83.6988	82.4143	81.960	89.601	83.8157	82.4551	81.9785
$\langle\delta(\vec{r}_3)\rangle$ (a.u.)	2.70	0.79	0.33	0.17	0	0	0	0
$\langle r_1\rangle$ (a.u.)	0.513365	1.04375	1.78881	2.7482	0.49704781	1.01990811	1.7570624	2.708506
$\langle r_1^2\rangle$ (a.u.)	0.434214	2.07419	6.4894	15.809	0.4023515	1.9710638	6.24715	15.336775
$\langle r_3\rangle$ (a.u.)	0.861278	1.91089	3.3965	5.3131	0.8376174	1.8653284	3.333798	5.234054
$\langle r_3^2\rangle$ (a.u.)	0.87165	4.1499	12.9797	31.618	0.8066643	3.9433448	12.49506	30.67406

[a] Denotes an extrapolated value.

TABLE X. Ionization energy and the expectation values of various operators for the low-lying excited S states of F VIII.

State	$2\,^1S$	$3\,^1S$	$4\,^1S$	$5\,^1S$	$2\,^3S$	$3\,^3S$	$4\,^3S$	$5\,^3S$
J_{nr} (cm^{-1})	178 9118.95	790 516	443 271^{a}	283 147^{a}	1 861 450.57	809 640.33	451 016.4	287 034.40
E_J (cm^{-1})	1797	647.4	296.6	159	2 379.2	805.84	360.3	190.57
$-\epsilon_M$ (cm^{-1})	−0.603	−0.190	−0.083	−0.04	−0.5209	−0.15309	−0.0642	−0.0327
J_{theor} (cm^{-1})	179 0916	791 164	443 568^{a}	283 306^{a}	1 863 829.2	810 446.01	451 376.6	287 224.93
$\langle\delta(\vec{r}_1)\rangle$ (a.u.)	127.1716	119.2898	117.3940	116.72	127.893	119.4428	117.4474	116.7472
$\langle\delta(\vec{r}_3)\rangle$ (a.u.)	4.03	1.18	0.49	0.25	0	0	0	0
$\langle r_1\rangle$ (a.u.)	0.451458	0.916094	1.56853	2.4085	0.4387801	0.89760023	1.5439277	2.377758
$\langle r_1^2\rangle$ (a.u.)	0.334685	1.59430	4.9825	12.131	0.3128850	1.5240245	4.81769	11.809714
$\langle r_3\rangle$ (a.u.)	0.755822	1.67525	2.9761	4.6541	0.7386442	1.64019825	2.9276294	4.592932
$\langle r_3^2\rangle$ (a.u.)	0.671670	3.18967	9.9656	24.262	0.6271478	3.0489107	9.63592	23.61979

[a] Denotes an extrapolated value.

TABLE XI. Ionization energy and the expectation values of various operators for the low-lying excited *S* states of Ne IX.

State	$2\,^1S$	$3\,^1S$	$4\,^1S$	$5\,^1S$	$2\,^3S$	$3\,^3S$	$4\,^3S$	$5\,^3S$
$J_{\rm nr}$(cm^{-1})	2 259 503.80	999 075	560 417[a]	358 052[a]	2 341 432.86	1 020 728.23	569 188.2	362 455.60
E_J(cm^{-1})	2 891	1040.3	476.5	255	3714.8	1264.58	566.7	300.14
$-\epsilon_M$(cm^{-1})	−0.646	−0.205	−0.089	−0.05	−0.5606	−0.16518	−0.0693	−0.0354
$J_{\rm theor}$(cm^{-1})	2 262 394	1 000 115	560 893[a]	358 307[a]	2 345 147.1	1 021 992.65	569 754.8	362 755.70
$\langle\delta(\vec{r}_1)\rangle$(a.u.)	174.87366	163.7660	161.0904	160.14	175.786	163.9597	161.1583	160.1736
$\langle\delta(\vec{r}_3)\rangle$(a.u.)	5.74	1.673	0.70	0.4	0	0	0	0
$\langle r_1\rangle$(a.u.)	0.4028899	0.816281	1.39659	2.1436	0.39275687	0.80152227	1.3769608	2.119069
$\langle r_1^2\rangle$(a.u.)	0.265839	1.263573	3.9455	9.601	0.2502741	1.2135586	3.82836	9.373443
$\langle r_3\rangle$(a.u.)	0.673368	1.491365	2.64833	4.1406	0.66061400	1.46361199	2.6097641	4.091844
$\langle r_3^2\rangle$(a.u.)	0.533377	2.52794	7.8914	19.203	0.5015528	2.4277493	7.65712	18.747156

[a] Denotes an extrapolated value.

TABLE XII. Ionization energy and the expectation values of various operators for the low-lying *P* states of He. $J_{\rm nr}$ denotes the nonrelativistic ionization energy, and $J_{\rm theor}=J_{\rm nr}+E_J-\epsilon_M$ is the total theoretical ionization energy (excluding the Lamb-shift correction).

State	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$	$2\,^3P_1$	$3\,^3P_1$	$4\,^3P_1$	$5\,^3P_1$
$J_{\rm nr}$(cm^{-1})	27 176.688	12 101.57	6 818.1	4 368.2	29 222.1537	12 745.576	7 093.40	4 509.8
E_J(cm^{-1})	0.46772	0.1734	0.080	0.04	−0.31480	−0.057	−0.017	−0.01
$-\epsilon_M$(cm^{-1})	−1.385197	−0.43767	−0.1882	−0.10	1.942588	0.55260	0.2273	0.11
$J_{\rm theor}$(cm^{-1})	27 175.771	12 101.30	6 818.1	4 368.1	29 223.7815	12 746.072	7 093.61	4 509.9
$\langle\delta(\vec{r}_1)\rangle$(a.u.)	1.274393	1.273628	1.27341	1.2733	1.258860	1.26912	1.27154	1.2724
$\langle\delta(\vec{r}_3)\rangle$(a.u.)	0.000736	0.000253	0.00011	0.0001	0	0	0	0
$\langle 1/r_1\rangle$(a.u.)	1.2317751	1.0549723	1.0310004	1.01987	1.133242422	1.05802279	1.032289	1.020534
$\langle r_1\rangle$(a.u.)	2.910684	6.67954	11.948	18.7	2.6739616	6.32113	11.469	18.112
$\langle r_1^2\rangle$(a.u.)	15.76565	91.873	304.1	757	13.21174	82.1098	279.93	709.2
$\langle 1/r_3\rangle$(a.u.)	0.24502387	0.10959669	0.06186	0.039681	0.26664131	0.1159290	0.064506	0.041025
$\langle r_3\rangle$(a.u.)	5.138328	12.63801	23.161	36.68	4.699955	11.93120	22.207	35.49
$\langle r_3^2\rangle$(a.u.)	31.59851	183.786	608.1	1514	26.64279	164.303	559.9	1418

TABLE XIII. Ionization energy and expectation values of various operators for the low-lying P states of Li II.

State	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$	$2\,^3P_1$	$3\,^3P_1$	$4\,^3P_1$	$5\,^3P_1$
$J_{\mathrm{nr}}(\mathrm{cm}^{-1})$	108 269.571	48 326.04	27 245.9	17 461.4	115 811.140	50 576.09	28 192.3	17 944.68
$E_J(\mathrm{cm}^{-1})$	5.6359	2.11	0.98	0.53	1.5164	1.052	0.555	0.32
$-\epsilon_M(\mathrm{cm}^{-1})$	−4.311064	−1.2662	−0.5310	−0.271	5.236925	1.34824	0.5386	0.268
$J_{\mathrm{theor}}(\mathrm{cm}^{-1})$	108 270.896	48 326.88	27 246.4	17 461.7	115 817.893	50 578.49	28 193.4	17 945.26
$\langle\delta(\vec{r}_1)\rangle$ (a.u.)	4.306571	4.2995	4.2980	4.298	4.235063	4.28063	4.29048	4.2938
$\langle\delta(\vec{r}_3)\rangle$ (a.u.)	0.00984	0.00335	0.0015	0.0008	0	0	0	0
$\langle 1/r_1\rangle$ (a.u.)	1.74657954	1.6101655	1.562114	1.539806	1.76071902	1.61419850	1.56378698	1.540655
$\langle r_1\rangle$ (a.u.)	1.5219320	3.40596	6.0407	9.425	1.4183667	3.253252	5.8376	9.172
$\langle r_1^2\rangle$ (a.u.)	4.041627	23.1063	76.22	189.7	3.465405	20.9837	71.04	179.46
$\langle 1/r_3\rangle$ (a.u.)	0.49277510	0.2205794	0.124382	0.07971	0.50888277	0.2242717	0.125795	0.080394
$\langle r_3\rangle$ (a.u.)	2.592469	6.33485	11.5947	18.359	2.4282528	6.04063	11.1928	17.854
$\langle r_3^2\rangle$ (a.u.)	8.07421	46.2205	152.46	379.4	7.046632	42.0049	142.09	358.9

TABLE XIV. Ionization energy and the expectation values of various operators for the low-lying P states of Be III.

State	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$	$2\,^3P_1$	$3\,^3P_1$	$4\,^3P_1$	$5\,^3P_1$
J_{nr} (cm^{-1})	243 771.334	108 846.12	61 359.2	39 318.8	257 861.082	112 935.72	63 065.2	40 186.93
E_J (cm^{-1})	24.621	9.40	4.41	2.4	16.491	7.71	3.78	2.1
$-\epsilon_M$ (cm^{-1})	−8.30468	−2.320	−0.957	−0.48	9.43590	2.3302	0.920	0.456
J_{theor} (cm^{-1})	243 787.650	108 853.19	61 362.6	39 320.7	257 887.009	112 945.76	63 069.9	40 189.5
$\langle\delta(\vec{r}_1)\rangle$ (a.u.)	10.21113	10.19104	10.1877	10.187	10.04770	10.1501	10.172	10.18
$\langle\delta(\vec{r}_3)\rangle$ (a.u.)	0.0413	0.0139	0.0062	0.003	0	0	0	0
$\langle 1/r_1\rangle$ (a.u.)	2.3709283	2.1656164	2.093331	2.059792	2.38642090	2.1699177	2.095102	2.06069
$\langle r_1\rangle$ (a.u.)	1.033819	2.28843	4.044	6.30	0.9779074	2.20714	3.9359	6.164
$\langle r_1^2\rangle$ (a.u.)	1.81053	10.263	33.83	84.2	1.59961	9.5011	31.98	80.5
$\langle 1/r_3\rangle$ (a.u.)	0.7458833	0.332992	0.18748	0.1200	0.7414210	0.330133	0.18609	0.1193
$\langle r_3\rangle$ (a.u.)	1.728490	4.2201	7.723	12.23	1.657146	4.06748	7.511	11.963
$\langle r_3^2\rangle$ (a.u.)	3.6015	20.527	67.66	168	3.26722	19.0221	63.97	161.1

TABLE XV. Ionization energy and the expectation values of various operators for the low-lying P states of B IV.

State	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$	$2\,^3P_1$	$3\,^3P_1$	$4\,^3P_1$	$5\,^3P_1$
J_{nr} (cm^{-1})	433 941.861	193 723.86	109 181.4	69 951.8	454 978.427	199 726.98	111 673.24	71 217.15
E_J (cm^{-1})	71.48	27.73	13.1	7	63.609	27.3	13.1	7
$-\epsilon_M$ (cm^{-1})	−12.60951	−3.4014	−1.3869	−0.6989	13.83023	3.3404	1.312	0.65
J_{theor} (cm^{-1})	434 000.73	193 748.18	109 193.1	69 958	455 055.866	199 757.6	111 687.7	71 225
$\langle\delta(\vec{r}_1)\rangle$ (a.u.)	19.94267	19.9029	19.897	19.90	19.65248	19.833	19.870	19.882
$\langle\delta(\vec{r}_3)\rangle$ (a.u.)	0.1104	0.0367	0.016	0.01	0	0	0	0
$\langle 1/r_1\rangle$ (a.u.)	2.9956172	2.7211345	2.624572	2.579788	3.01170738	2.7255380	2.6263773	2.58070
$\langle r_1\rangle$ (a.u.)	0.783387	1.72358	3.039	4.730	0.7487084	1.673594	2.9732	4.648
$\langle r_1^2\rangle$ (a.u.)	1.02199	5.7657	19.00	47.3	0.922869	5.41187	18.144	45.6
$\langle 1/r_3\rangle$ (a.u.)	1.0016061	0.445915	0.25074	0.1604	0.9707984	0.435243	0.24608	0.1580
$\langle r_3\rangle$ (a.u.)	1.294670	3.16214	5.788	9.17	1.2618938	3.07087	5.6586	9.00
$\langle r_3^2\rangle$ (a.u.)	2.02543	11.5303	38.00	94.6	1.889931	10.8357	36.29	91.2

TABLE XVI. Ionization energy and expectation values of various operators for the low-lying P states of Cv.

State	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$	$2\,^3P_1$	$3\,^3P_1$	$4\,^3P1$	$5\,^3P_1$
J_{nr} (cm^{-1})	678 876.882	302 975.53	170 717.7	109 362.6	707 051.391	310 923.18	174 005.71	111 029.90
E_J (cm^{-1})	165.36	64.95	31	17	169.89	70.2	33.5	18
$-\epsilon_M$ (cm^{-1})	−18.494239	−4.8627	−1.9666	−0.9876	19.86151	4.7319	1.852	0.92
J_{theor} (cm^{-1})	679 023.75	303 035.62	170 747	109 378	707 241.14	310 998.1	174 041.0	111 049
$\langle\delta(\vec{r}_1)\rangle$ (a.u.)	34.45597	34.3900	34.38	34.38	34.00445	34.283	34.340	34.36
$\langle\delta(\vec{r}_3)\rangle$ (a.u.)	0.2328	0.077	0.034	0.02	0	0	0	0
$\langle 1/r_1\rangle$ (a.u.)	3.62044722	3.2766740	3.155819	3.099788	3.63685106	3.28112533	3.1576398	3.10071
$\langle r_1\rangle$ (a.u.)	0.6308163	1.38256	2.4348	3.787	0.6072863	1.348828	2.3901	3.731
$\langle r_1^2\rangle$ (a.u.)	0.655334	3.6859	12.145	30.2	0.6011590	3.49409	11.683	29.33
$\langle 1/r_3\rangle$ (a.u.)	1.2587021	0.559045	0.31407	0.2008	1.1987913	0.540034	0.30595	0.19666
$\langle r_3\rangle$ (a.u.)	1.0342843	2.52780	4.627	7.33	1.0201076	2.467976	4.5409	7.219
$\langle r_3^2\rangle$ (a.u.)	1.294884	7.3704	24.29	60.5	1.233212	6.99603	23.369	58.66

TABLE XVII. Ionization energy and expectation values of various operators for the low-lying P states of N VI.

State	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$	$2\,^3P_1$	$3\,^3P_1$	$4\,^3P_1$	$5\,^3P_1$
J_{nr} (cm^{-1})	978 624.519	436 609.22	245 970.9	157 552.5	1 014 043.119	446 516.96	250 060.04	159 624.07
E_J (cm^{-1})	330.51	131.10	62	34	370.37	150	71	39
$-\epsilon_M$ (cm^{-1})	−23.139706	−5.9673	−2.3988	−1.201	24.51093	5.7858	2.260	1.12
J_{theor} (cm^{-1})	978 931.88	436 734.34	246 031	157 585	1 014 438.00	446 673	250 133	159 664
$\langle\delta(\vec{r}_1)\rangle$ (a.u.)	54.7059	54.6072	54.60	54.59	54.0586	54.4567	54.537	54.56
$\langle\delta(\vec{r}_3)\rangle$ (a.u.)	0.424	0.139	0.061	0.03	0	0	0	0
$\langle 1/r_1\rangle$ (a.u.)	4.24534478	3.8322216	3.68707	3.61979	4.26193306	3.83669881	3.6888969	3.62071
$\langle r_1\rangle$ (a.u.)	0.5280650	1.15427	2.0309	3.157	0.5110783	1.130019	1.9988	3.1175
$\langle r_1^2\rangle$ (a.u.)	0.455645	2.5574	8.427	20.98	0.4228951	2.44206	8.149	20.44
$\langle 1/r_3\rangle$ (a.u.)	1.5165943	0.672271	0.37742	0.2413	1.4260594	0.644662	0.36575	0.23528
$\langle r_3\rangle$ (a.u.)	0.8608323	2.10526	3.8541	6.105	0.8565402	2.063511	3.7925	6.026
$\langle r_3^2\rangle$ (a.u.)	0.898146	5.1134	16.85	42.0	0.868558	4.88963	16.300	40.88

TABLE XVIII. Ionization energy and expectation values of various operators for the low-lying P states of O VII.

State	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$	$2\,^3P_1$	$3\,^3P_1$	$4\,^3P_1$	$5\,^3P_1$
J_{nr} (cm^{-1})	1 333 204.452	594 626.38	334 941.0	214 521.5	1 375 931.947	606 502.98	339 833.96	216 998.43
E_J (cm^{-1})	596.26	238.3	114 ± 2	62 ± 2	708.14	283	134	72.8(+4)
$-\epsilon_M$ (cm^{-1})	−27.823945	−7.0674	−2.8278	−1.413	29.19196	6.8450	2.669	1.317
J_{theor} (cm^{-1})	1333 772.89	594 857.6	335 052 ± 2	214 582 ± 2	1 376 669.28	606 793	339 970	217 072.6(+4)
$\langle\delta(\vec{r}_1)\rangle$ (a.u.)	81.6473	81.509	81.49	81.49	80.7699	81.308	81.42	81.45
$\langle\delta(\vec{r}_3)\rangle$ (a.u.)	0.709	0.228	0.099	0.05	0	0	0	0
$\langle 1/r_1\rangle$ (a.u.)	4.87027850	4.3877730	4.21832	4.13979	4.88698421	4.39226543	4.2201513	4.14071
$\langle r_1\rangle$ (a.u.)	0.4541356	0.990728	1.7419	2.707	0.44130647	0.9724680	1.71778	2.6773
$\langle r_1^2\rangle$ (a.u.)	0.3350408	1.87756	6.186	15.41	0.3137625	1.802938	6.007	15.05
$\langle 1/r_3\rangle$ (a.u.)	1.7749857	0.785547	0.44078	0.2817	1.6529019	0.749195	0.42552	0.27389
$\langle r_3\rangle$ (a.u.)	0.7370762	1.80367	3.3023	5.231	0.7383823	1.773194	3.2563	5.172
$\langle r_3^2\rangle$ (a.u.)	0.659119	3.75381	12.373	30.81	0.6449831	3.60994	12.016	30.11

TABLE XIX. Ionization energy and expectation values of various operators for the low-lying P states of F VIII.

State	$2\,^1P$	3^1P	4^1P	5^1P	2^3P_1	3^3P_1	4^3P_1	5^3P_1
J_{nr} (cm^{-1})	1 742 631.753	777 029.43	437 629.0	280 270.0	1 792 710.688	790 880.30	443 327.32	283 153.02
E_J (cm^{-1})	997.1	401.0	192 ± 2	105 ± 2	1 234.32	489	231	125.4 (+6)
$-\epsilon_M$ (cm^{-1})	−30.788733	−7.7262	−3.0801	−1.537	32.07742	7.4839	2.915	1.44
J_{theor} (cm^{-1})	1 743 598.1	777 422.7	437 818 ± 2	280 373 ± 2	1 793 977.09	791 376	443 561	283 279.9(+ 6)
$\langle\delta(\vec{r}_1)\rangle$ (a.u.)	116.2352	116.051	116.03	116.0	115.0932	115.792	115.93	116.0
$\langle\delta(\vec{r}_3)\rangle$ (a.u.)	1.076	0.349	0.15	0.08	0	0	0	0
$\langle 1/r_1\rangle$ (a.u.)	5.49523322	4.9433261	4.74957	4.65979	5.51201822	4.94782829	4.7514042	4.660714
$\langle r_1\rangle$ (a.u.)	0.3983838	0.867801	1.5250	2.370	0.38835698	0.8535621	1.50616	2.3462
$\langle r_1^2\rangle$ (a.u.)	0.2566740	1.43667	4.734	11.79	0.2420813	1.385666	4.6112	11.550
$\langle 1/r_3\rangle$ (a.u.)	2.0337096	0.898851	0.50414	0.3221	1.8794734	0.8536693	0.48526	0.31249
$\langle r_3\rangle$ (a.u.)	0.6443658	1.577623	2.8886	4.576	0.64897284	1.554611	2.85305	4.5303
$\langle r_3^2\rangle$ (a.u.)	0.5041309	2.87219	9.467	23.58	0.4979664	2.77445	9.2237	23.10

TABLE XX. Ionization energy and expectation values of various operators for the low-lying P states of Ne IX.

State	$2\,^1P$	3^1P	$4\,^1P$	$5\,^1P$	$2\,^3P_1$	$3\,^3P_1$	$4\,^3P_1$	$5\,^3P_1$
J_{nr} (cm^{-1})	2 206 905.235	983 815.18	554 032.7	354 796.7	2 264 364.765	999 643.80	560 537.46	358 086.21
E_J (cm^{-1})	1 572.6	635.6	305 ± 2	167 ± 2	2 008.05	790	372	202.3(+8)
$-\epsilon_M$ (cm^{-1})	- 37.198334	−9.2424	−3.6735	−1.831	38.55028	8.9590	3.487	1.72
J_{theor} (cm^{-1})	2 208 440.6	984 441.6	554 334 ± 2	354 962 ± 2	2 266 411.37	1 000 442	560 913	358 290.2(+8)
$\langle\delta(\vec{r})\rangle$ (a.u.)	159.4244	159.188	159.16	159.2	157.9836	158.864	159.04	159.1
$\langle\delta(\vec{r}_3)\rangle$ (a.u.)	1.569	0.507	0.22	0.12	0	0	0	0
$\langle 1/r_1\rangle$ (a.u.)	6.12020095	5.4988801	5.28082	5.17979	6.13704197	5.50338892	5.2826562	5.180715
$\langle r_1\rangle$ (a.u.)	0.35483492	0.772024	1.35611	2.1069	0.34678501	0.7606139	1.34102	2.0881
$\langle r_1^2\rangle$ (a.u.)	0.2029006	1.13461	3.7385	9.312	0.19246321	1.098225	3.6511	9.141
$\langle 1/r_3\rangle$ (a.u.)	2.2926656	1.012172	0.56751	0.3625	2.1058619	0.9581034	0.544991	0.35108
$\langle r_3\rangle$ (a.u.)	0.5723358	1.401907	2.5670	4.067	0.57893221	1.3840687	2.53876	4.0303
$\langle r_3^2\rangle$ (a.u.)	0.3979740	2.26821	7.477	18.62	0.3961106	2.198905	7.3032	18.28

TABLE XXI. Ionization energies for the higher excited ^1S states of He. J_{nr} denotes the nonrelativistic ionization energy, $E_J - \epsilon_M$ the contribution from the mass-polarization and relativistic corrections, and J_{theor} the total theoretical ionization energy. The results are given in units of cm^{-1}.

State	$6\,^1S$	$7\,^1S$	$8\,^1S$	$9\,^1S$	$10\,^1S$	$11\,^1S$	$12\,^1S$	$13\,^1S$	$14\,^1S$	$15\,^1S$
J_{nr} (method C)	3195.48	2331.44	1775.72	1397.34	1128.2	929.8	779.6	663.0	570.7	496.4
J_{nr} (C, extrapolated)	3195.78	2331.75	1776.07	1397.71	1128.5	930.2	780.0	663.4	571.1	496.8
J_{nr} (method D)	3195.78	2331.75	1776.08	1397.74	1128.5	930.2	779.9	663.3	570.9	496.7
J_{nr} (D, extrapolated)	3195.79	2331.77	1776.10	1397.76	1128.6	930.3	780.1	663.4	571.2	496.9
J_{nr} (value adopted)	3195.79	2331.77	1776.10	1397.76	1128.6	930.3	780.0	663.4	571.2	496.9
$E_J - \epsilon_M$	0.01	0.01								
J_{theor}	3195.80	2331.78	1776.10	1397.76	1128.6	930.3	780.0	663.4	571.2	496.9

states, owing, no doubt, to the inadequacy of the use of equal values for the screening constants ξ and η for the two electrons.

The relativistic and mass-polarization corrections are all of the form $\int \psi O_p \psi \, d\vec{r}_1 d\vec{r}_2$, where ψ is the solution of (1), and O_p is an operator. As before, the integration over the angular coordinates may be carried out directly, and we are left with an integration over r_1, r_2, and r_3. For the S states, these integrations were also carried out in terms of the perimetric coordinates. For the P states, the expressions involved would have been too complicated, and the expression (4) for the wave function was therefore first converted into a triple series in powers of r_1, r_2, and r_3. Even in terms of these coordinates, the integrals involved were of considerable complication, and an interpretive programming scheme was designed in order to evaluate them on the computer.

The total theoretical ionization potential, which we denote by J_{theor}, is obtained by adding these corrections to the nonrelativistic value, and is computed in the form $J_{\text{theor}} = J_{\text{nr}} + E_J - \epsilon_M$, where all quantities are in units of cm^{-1}. $-\epsilon_M$ and E_J denote the contributions from the mass-polarization and relativistic corrections, respectively, and the nonrelativistic ionization potential J_{nr} is given by $J_{\text{nr}} = -(2E + Z^2)R_M$, where E is the eigenvalue of Eq. (1) in a.u. R_M denotes the Rydberg constant for the isotope in question.

III. RESULTS

A. Nonrelativistic Eigenvalues

For the S states, nonrelativistic eigenvalues and wave functions were obtained for the eight states $n\,^1S$, $n\,^3S$, $n = 2$ to 5 for the atoms $Z = 2$ to 10, and also for some of the higher excited states of He.

For the atoms other than He, type-D expansions containing up to 220 terms were first used. It was found that a loss of accuracy due to cancellation prevented the determination of the eigenvalue and corresponding wave function if the expansion contained too many terms.

The loss of accuracy was most serious for the lowest-lying states of a given ion, and the accuracy also deteriorated for a given state as the atomic number increased. Thus, for example, in the case of the $5\,^1S$ and $5\,^3S$ states, eigenvalues were obtained without any difficulty for expansions containing up to 220 terms, whereas for the $2\,^1S$ and $2\,^3S$ states, the expansion could only be carried out up to 120 terms in the case of Li^+, and up to order 56 for $Z > 3$. In view of these difficulties, it was decided to repeat the computations for the S states using method C, in which the parameter ξ has the fixed values $(-2E - Z^2)^{1/2}$. The loss of accuracy was found to be much less severe than in the case of method D, and we were able to carry the expansions up to order 364 in all cases except for the $2\,^1S$ state, for which up to 220 terms could be included, and the $2\,^3S$ state, for which up to 220 terms could be included in the case of Li^+, and up to 120 terms for larger values of Z.

The results obtained using a type-D expansion converge more readily. Thus, for example, a type-D expansion of order 220 for a given state yields roughly the same result as a type-C expansion of order 364. On the other hand, it was generally found that the slower convergence of the type-C expansion is offset by the fact that one can include a larger number of terms before loss of accuracy sets in, so that the final eigenvalue obtained is about the same in either case. These points are illustrated in Table I, in which the values of J_{nr} obtained using C- and D-type expansions are compared with one another for the $2\,^1S$, $2\,^3S$, $5\,^1S$, and $5\,^3S$ states of He, C v, and Ne ix. The table also contains the optimum values of ξ obtained for the type-D expansions.

In view of the particular importance of He and Li^+, we decided to carry out more extensive calculations for these two atoms. In the case of the $n\,^1S$ and $n\,^3S$ states, $n = 3$, 4, and 5, the type-C ex-

TABLE XXII. Ionization energies for the higher excited ^3S states of He. J_{nr} denotes the nonrelativistic ionization energy, $E_J - \epsilon_M$ the contribution from the mass-polarization and relativistic corrections, and J_{theor} the total theoretical ionization energy. The results are given in units of cm^{-1}.

State	$6\,^3S$	$7\,^3S$	$8\,^3S$	$9\,^3S$	$10\,^3S$	$11\,^3S$	$12\,^3S$	$13\,^3S$	$14\,^3S$	$15\,^3S$	$16\,^3S$	$17\,^3S$
J_{nr} (method C)	3374.496	2442.398	1849.284	1448.661	1165.407	957.785	801.059	679.851	584.22	507.39	444.81	393.06
J_{nr} (C, extrapolated)		2442.398	1849.285	1448.667	1165.426	957.811	801.111	679.941	584.32	507.53	444.95	393.25
J_{nr} (method D)	3374.498	2442.400	1849.285	1448.666	1165.424	957.808	801.108	679.938	584.32	507.53	444.93	393.24
J_{nr} (D, extrapolated)			1849.285	1448.666	1165.424	957.810	801.110	679.942	584.32	507.54	444.96	393.27
J_{nr} (value adopted)	3374.50	2442.40	1849.285	1448.666	1165.424	957.810	801.110	679.94	584.32	507.54	444.96	393.27
$E_J - \epsilon_M$	0.055	0.034	0.023	0.016	0.01	0.01						
J_{theor}	3374.61	2442.43	1849.308	1448.682	1165.44	957.82	801.11	679.94	584.32	507.54	444.96	393.27

TABLE XXIII. Conversion factors used in the calculations. R_M is the Rydberg constant and m/M the ratio of the mass of an electron to that of the appropriate nuclear isotope.

Z	Isotope	R_M	$\alpha^2 R_M$	$2(m/M)R$
2	He^4	109 722.267	5.842755	30.08387
3	Li^7	109 728.727	5.843099	17.163109
4	Be^9	109 730.628	5.843200	13.3619
5	B^{11}	109 731.840	5.843264	10.9381
6	C^{12}	109 732.291	5.843288	10.0355
7	N^{14}	109 733.009	5.843327	8.6000
8	O^{16}	109 733.544	5.843355	7.5290
9	F^{19}	109 734.140	5.843387	6.3387
10	Ne^{20}	109 734.297	5.843395	6.0235

pansions were carried up to as high an order as possible. Up to 1540 terms were included, with a corresponding improvement in the accuracy of the results. For He, we also decided to improve and extend the previous calculations by one of us for the higher excited states.[23] As will be seen from the results in Table I, the higher the excited state lies, the poorer is the convergence of the eigenvalue. We nevertheless decided to extend the calculations to as high an excited state as possible. The previous work treated the states up to $9\,^1S$ and $9\,^3S$ using expansions up to order 220. By using type-C and -D expansions containing up to 2300 terms, improved results were obtained, and we were also able to extend the calculations up to the $15\,^1S$ and $17\,^3S$ states. Again, the results using type-D expansions were found to converge more rapidly.

Calculations were also carried out for the $2\,^1S$ states for all values of Z using method B.[22] Expansions containing up to 1078 terms were used, resulting in considerably more accurate eigenvalues for this state than could be obtained using either methods C or D. Method B is, however, not suitable for use in the case of the higher excited states.

In the case of the P states, the nonrelativistic eigenvalues and the corresponding wave functions were obtained using type-D expansions of order 20, 56, 120, 220, and 364 for each of the eight states $n\,^1P$, $n\,^3P$, $n = 2$ to 5 in the cases $Z = 2$ to 10. The expansion was also carried up to order 560 ($\Omega = 13$) in the case of He, and for the $5\,^1P$ and $5\,^3P$ states for other values of Z. For each state, the eigenvalue was optimized with respect to the parameter ξ in the case of the expansions containing up to 220 terms, and the optimum values thus obtained were extrapolated approximately to obtain suitable values of ξ for use in the expansion of orders 364 and 560. Optimization with respect to ξ for an expansion of order 364 or 560 would have been expensive in terms of computer time, and was not felt to be necessary in view of the fact that the ei-

TABLE XXIV. Total theoretical ionization energy J_{theor} in cm^{-1} for singlet states of the He isoelectronic sequence. The values include the contributions from the mass-polarization and relativistic corrections, but not the Lamb-shift correction.

State Z	$2\,^1S$	$3\,^1S$	$4\,^1S$	$5\,^1S$	$2\,^1P$	$3\,^1P$	$4\,^1P$	$5\,^1P$
2	32 033.321	13 445.8	7 370.4	4 647.1	27 175.771	12 101.30	6 818.1	4 368.1
3	118 705.575	51 301.6	28 482.9	18 089.8	108 270.896	48 326.88	27 246.4	17 461.7
4	260 067.3	113 541	63 319	40 316	243 787.650	108 853.19	61 362.6	39 320.7
5	456 269.6	200 189	111 884	71 329	434 000.73	193 748.18	109 193.1	69 958
6	707 386.8	311 255	174 183	111 130	679 023.75	303 035.62	170 747	109 378
7	1 013 488.3	446 759	250 224	159 723	978 931.88	436 734.34	246 031	157 585
8	1 374 639	606 720	340 015	217 113	1 333 772.89	594 857.6	335 052 ± 2	214 582 ± 2
9	1 790 916	791 164	443 568	283 306	1 743 598.1	777 422.7	437 818 ± 2	280 373 ± 2
10	2 262 394	1 000 115	560 893	358 307	2 208 440.6	984 441.6	554 334 ± 2	354 962 ± 2

TABLE XXV. Total theoretical ionization energy J_{theor} in cm^{-1} for triplet states of the He isoelectronic sequence. The values include the contribution from the mass-polarization and relativistic corrections, but not the Lamb-shift correction.

State Z	$2\,^3S$	$3\,^3S$	$4\,^3S$	$5\,^3S$	$2\,^3P_1$	$3\,^3P_1$	$4\,^3P_1$	$5\,^3P_1$
2	38 454.8274	15 073.909	8 012.568	4 963.68	29 223.7815	12 746.072	7 093.61	4 509.9
3	134 045.260	55 325.094	30 097.79	18 894.8	115 817.893	50 578.49	28 193.4	17 945.26
4	284 744.3	120 060.26	65 947.5 ± ?	41 631.02	257 887.009	112 945.76	63 069.9	40 189.5
5	490 443.8	209 231.69	115 538.1 ± ?	73 159.27	455 055.866	199 757.6	111 687.7	71 225
6	751 149.0	322 838.13	178 868.4 ± ?	113 478.52	707 241.14	310 998.1	174 041.0	111 049
7	1 066 906.9	460 895.21	255 945.2	162 592.56	1 014 438.00	446 673	250 133	159 664
8	1 437 774.7	623 422.21	346 777.2	220 505.84	1 376 669.28	606 793	339 970	217 073 ± ?
9	1 863 829.2	810 446.01	451 376.6	287 224.93	1 793 977.09	791 376	443 561	283 280 ± ?
10	2 345 147.1	1 021 992.65	569 754.8	362 755.70	2 266 411.37	1 000 442	560 913	358 290 ± ?

genvalue E is comparatively insensitive to small changes in the value of this parameter. In order to illustrate the convergence of the eigenvalue as the number of terms in the expansion is increased, we have listed the values of $J_{\rm nr}$ for the $2\,^1P$, $2\,^3P$, $5\,^1P$, and $5\,^3P$ states of He, C v, and Ne ix using different lengths of expansion in Table II. The table also contains the value of ξ adopted in each case. For the $2\,^3P$ state of He only, the parameter η was given values differing from $\eta = Z$.[24]

B. Mass-Polarization and Relativistic Corrections

Having obtained the nonrelativistic wave functions, we could then compute the expectation values of various operators, and hence calculate the mass-polarization and relativistic corrections. Full details of the definitions, formula, and methods used have been given in previous publications.[19,24] For the S states, the expectation values were computed using type-C wave functions of orders up to 364. In the case of the P states, these calculations require a large amount of computer time, and they were therefore only carried out for wave functions of orders up to 220, except for He and Li$^+$, where expansions containing up to 364 or 560 terms were used.

C. Total Ionization Energy

The final results obtained for the S states, apart from the higher excited states of He, are listed in Tables III–XI, and for the P states in Tables XII–XX. The values of $J_{\rm nr}$, E_J, $-\epsilon_M$ and $J_{\rm theor} = J_{\rm nr} + E_J - \epsilon_M$ are listed in cm^{-1}, and the expectation values in a.u. The results listed in these tables are those obtained using the largest expansion employed, with the exception of those entries marked with an asterisk, which are extrapolated values, i.e., the values which would have been obtained if an infinite number of terms were to have been included in the expansion of the wave function. The other results listed are estimated to differ by not more than 1, or occasionally 2, in the last digit quoted from the extrapolated value, unless otherwise stated. Error estimates have been included in the tables in two kinds of situations. First, if the extrapolated value is liable to differ from the value listed by 2 or more in the last digit quoted, but on the other hand we do not wish to quote the results to one less significant figure. In this case, the value is followed by the estimated error. Thus, for example, in Table XX, we quote the value 305 ± 2 for E_J for the $4\,^1P$ state of Ne ix. This means that the value 305 cm^{-1} was obtained with the largest expansion employed, and we estimate the extrapolated value to lie between 303 and 307 cm^{-1}. Second, there are cases where the behavior of the differences as the number of terms in the expansion is increased does

TABLE XXVI. Fine-structure splitting for the ^3P states. The quantities $\Delta\nu_{01}$ and $\Delta\nu_{21}$ are to be added to the total ionization energy $J_{\rm theor}$ for the $J=1$ level (listed in Table XXV) in order to obtain $J_{\rm theor}$ for the $J=0$ and $J=2$ levels, respectively.

State	$2\,^3P$		$3\,^3P$		$4\,^3P$		$5\,^3P$	
Z	$\Delta\nu_{01}$ (cm^{-1})	$\Delta\nu_{21}$ (cm^{-1})	$\Delta\nu_{01}$ (cm^{-1})	$\Delta\nu_{21}$ (cm^{-1})	$\Delta\nu_{01}$ (cm^{-1})	$\Delta\nu_{21}$ (cm^{-1})	$\Delta\nu_{01}$ (cm^{-1})	$\Delta\nu_{21}$ (cm^{-1})
2	−0.98784	0.07653	−0.27063	0.02199	−0.1103	0.0090	−0.0556	0.0048
3	−5.18997	−2.08542	−1.3460	−0.6258	−0.539	−0.264	−0.270	−0.135
4	−11.5177	−14.8420	−2.827	−4.394	−1.11	−1.85	−0.55	−0.94
5	−15.9797	−52.3959	−3.468	−15.458	−1.29	−6.50	−0.63	−3.31
6	−11.670	−134.799	−1.157	−39.728	−0.18	−16.70	−0.0	−8.5
7	11.241	−287.958	7.08	−84.85	3.5	−35.7	1.9	−18.2
8	65.513	−543.638	25.10	−160.20	11.3	−67.4	6.0	−34.4
9	166.834	−939.460	57.61	−276.91	25.4	−116.5	13.2	−59.5
10	333.816	−1518.898	110.19	−447.81	48.0	−188.4	24.9	−96.3

TABLE XXVII. Theoretical and experimental wavelengths for transitions from the ground state for $Z=2$ to 5. λ_{nr} denotes the nonrelativistic value, λ_{theor} the value including the mass-polarization and relativistic corrections, and λ_{tot} the value including the Lamb-shift correction for the $1\,^1S$ level.

	Transition	λ_{nr} (Å)	λ_{theor} (Å)	λ_{tot} (Å)	λ_{expt} (Å)	Ref.
He I	$1\,^1S-2\,^3P_1$	591.3829	591.4072	591.4119	591.4121 ± 0.0005 591.4117	6 25
	$1\,^1S-2\,^1P$	584.3147	584.3298	584.3343	584.3339 ± 0.0005 584.3340	6 25
	$1\,^1S-3\,^1P$	537.0114	537.0260	537.0299	537.0293 ± 0.0005 537.0296	6 25
Li II	$1\,^1S-2\,^1P$	199.2813	199.2760	199.2791	199.280 ± 0.003	2
	$1\,^1S-3\,^1P$	178.0162	178.0118	178.0143	178.014 ± 0.003	2
	$1\,^1S-4\,^1P$	171.5776	171.5734	171.5757	171.575 ± 0.004	2
Be III	$1\,^1S-2\,^1P$	100.2600	100.2507	100.2535	100.2552 ± 0.0015 100.254 ± 0.001	12 2
	$1\,^1S-3\,^1P$	88.3134	88.3054	88.3075	88.314 ± 0.002	2
	$1\,^1S-4\,^1P$	84.7588	84.7512	84.7532	84.758 ± 0.003	2
	$1\,^1S-5\,^1P$	83.2044	83.1970	83.1989	83.202 ± 0.003	2
B IV	$1\,^1S-2\,^3P_1$	61.0977	61.0869	61.0882	61.088 ± 0.002	4
	$1\,^1S-2\,^1P$	60.3224	60.3111	60.3135	60.3144 ± 0.0010	12
	$1\,^1S-3\,^1P$	52.6876	52.6781	52.6800	52.679 ± 0.002 52.682 ± 0.002 52.6853 ± 0.0020	2 4 12
	$1\,^1S-4\,^1P$	50.4408	50.4318	50.4335	50.4347 ± 0.0010	12
	$1\,^1S-5\,^1P$	49.4621	49.4533	49.4549	49.4549 ± 0.0012	12

not enable us to extrapolate with any degree of confidence. In this case, we have listed the value obtained using the largest expansion, followed by the difference, *in brackets*, between this value and that obtained with the aid of the expansion of next lower order. Thus, for example, in Table V, we quote the value 65 938.34(+2) for J_{nr} for the $4\,^3S$ state of Be III. This means that the values 65 938.32 and 65 938.34 were obtained from expansions of order 220 and 364, respectively, but we cannot make a completely reliable estimate of the extrapolated value.

TABLE XXVIII. Theoretical and experimental wavelengths for transitions from the ground state for $Z=6$ to 9. λ_{nr} denotes the nonrelativistic value, λ_{theor} the value including the mass-polarization and relativistic corrections, and λ_{tot} the value including the Lamb-shift correction for the $1\,^1S$ level.

	Transition	λ_{nr} (Å)	λ_{theor} (Å)	λ_{tot} (Å)	λ_{expt} (Å)	Ref.
C V	$1\,^1S-2\,^3P_1$	40.7397	40.7277	40.7299	40.7306 ± 0.0006	12
	$1\,^1S-2\,^1P$	40.2774	40.2650	40.2671	40.2679 ± 0.0008	12
	$1\,^1S-3\,^1P$	34.9811	34.9707	34.9723	34.9728 ± 0.0008	12
	$1\,^1S-4\,^1P$	33.4343	33.4244	33.4259	33.4257 ± 0.0008	12
	$1\,^1S-5\,^1P$	32.7622	32.7526	32.7540	32.7542 ± 0.0010	12
N VI	$1\,^1S-2\,^3P_1$	29.0948	29.0820	29.0840	29.084 ± 0.002	4
	$1\,^1S-2\,^1P$	28.7980	28.7848	28.7867	28.787 ± 0.002	4
	$1\,^1S-3\,^1P$	24.9098	24.8988	24.9002	24.898 ± 0.002	4
	$1\,^1S-4\,^1P$	23.7806	23.7701	23.7714	23.771 ± 0.002	4
O VII	$1\,^1S-2\,^3P_1$	21.8148	21.8015	21.8033	21.804 ± 0.002	4
	$1\,^1S-2\,^1P$	21.6133	21.5995	21.6012	21.6020 ± 0.0010	12
	$1\,^1S-3\,^1P$	18.6381	18.6266	18.6280	18.627 ± 0.002	4
	$1\,^1S-4\,^1P$	17.7777	17.7668	17.7680	17.768 ± 0.002	4
	$1\,^1S-5\,^1P$	17.4051	17.3945	17.3957	17.396 ± 0.002	4
F VIII	$1\,^1S-2\,^3P_1$	16.9617	16.9480	16.9496	16.951 ± 0.002	4
	$1\,^1S-2\,^1P$	16.8188	16.8045	16.8061	16.807 ± 0.002	4
	$1\,^1S-3\,^1P$	14.4690	14.4572	14.4584	14.458 ± 0.002	4

TABLE XXIX. Theoretical and experimental wavelengths for transitions of the type $2\,^1S-2\,^1P$ and $2\,^3S-2\,^3P$. λ_{nr} denotes the nonrelativistic value, λ_{theor} the value including the mass-polarization and relativistic corrections, and λ_{tot} the value including an estimate of the Lamb-shift correction for the $2\,^1S$ and $2\,^3S$ levels.

Transition		λ_{nr} (Å)	λ_{theor} (Å)	λ_{tot} (Å)	λ_{expt} (Å)	Ref.
He I	$2\,^1S-2\,^1P$	20590.88	20586.51	20586.95	20586.92	25
Li II	$2\,^1S-2\,^1P$	9587.86	9583.43	9584.06	9584.04 ± 0.10	8
Be III	$2\,^1S-2\,^1P$	6149.1	6142.7	6143.5	6142.9	5
B IV	$2\,^3S-2\,^3P_0$	2834.39	2824.55	2825.25	2825.40	5
C V	$2\,^3S-2\,^3P_0$		2276.89	2277.84	2277.96	11
C V	$2\,^3S-2\,^3P_1$	2289.20	2277.49	2278.44	2278.63	11
C V	$2\,^3S-2\,^3P_2$		2270.52	2271.46	2271.59	11
N VI	$2\,^3S-2\,^3P_0$		1906.30	1907.53	1907.87	9
N VI	$2\,^3S-2\,^3P_1$	1921.12	1905.89	1907.12	1907.34	9
N VI	$2\,^3S-2\,^3P_2$		1895.49	1896.70	1896.32	9
O VII	$2\,^3S-2\,^3P_0$		1638.27	1639.82	1639.58 ± 0.08	10
O VII	$2\,^3S-2\,^3P_1$	1655.56	1636.52	1638.06	1637.96 ± 0.08	10
O VII	$2\,^3S-2\,^3P_2$		1622.09	1623.60	1623.29 ± 0.08	10

The results obtained for the higher excited states of He are listed in cm^{-1} in Tables XXI and XXII. For each state, we list the value of J_{nr} obtained with the largest expansion used, as well as the extrapolated value, for both C- and D-type expansions. For the $6\,^3S$ state (C- and D-type expansions) and the $7\,^3S$ state (type D), no reliable extrapolation could be made, but the value from the next-lowest-

TABLE XXX. Theoretical and experimental wavelengths for transitions between excited S and P states. λ_{nr} denotes the nonrelativistic value, λ_{theor} the value including the mass-polarization and relativistic corrections, and λ_{tot} the value including estimates of the Lamb-shift correction for the $2\,^1S$ or $2\,^3S$ states.

Transition		λ_{nr} (Å)	λ_{theor} (Å)	λ_{tot} (Å)	λ_{expt} (Å)	Ref.
Li II	$3\,^1P-4\,^1S$	5039.3	5039.3		5039.32	7
Li II	$2\,^1P-3\,^1S$	1755.30	1755.33		1755.332	7
Li II	$3\,^1P-5\,^1S$	3307.24	3307.20		3307.236	7
Li II	$3\,^1S-4\,^1P$	4157.40	4157.11		4157.619	7
C V	$2\,^1S-3\,^1P$	247.437	247.310	247.316	247.31 ± 0.02	11
C V	$2\,^3S-3\,^3P_0$	227.370	227.194	227.204	227.192 ± 0.005	11
C V	$2\,^3S-3\,^3P_1$		227.195	227.204		
C V	$2\,^3S-3\,^3P_2$		227.174	227.184		
C V	$2\,^3S-4\,^3P_{0,1}$	173.392	173.278	173.283	173.281 ± 0.005	11
C V	$2\,^3S-4\,^3P_2$		173.273	173.278		
C V	$2\,^3S-5\,^3P_{0,1}$	156.322	156.226	156.230	156.233 ± 0.01	11
C V	$2\,^3S-5\,^3P_2$		156.223	156.228		
C V	$2\,^3P_0-3\,^3S$	260.180	260.152		260.136 ± 0.01	11
C V	$2\,^3P_1-3\,^3S$		260.144			
C V	$2\,^3P_2-3\,^3S$		260.235		260.229 ± 0.01	11
C V	$3\,^3S-4\,^3P_{0,1}$	672.51	672.06		672.0 ± 1.0	11
C V	$3\,^3S-4\,^3P_2$		671.98			
C V	$3\,^3P_0-4\,^3S$	756.91	756.84		756.0 ± 1.0	11
C V	$3\,^3P_1-4\,^3S$		756.83			
C V	$3\,^3P_2-4\,^3S$		757.06			
O VII	$2\,^3S-3\,^3P_0$	120.5064	120.3432	120.3516	120.331	5
O VII	$2\,^3S-3\,^3P_1$		120.3396	120.3479		
O VII	$2\,^3S-3\,^3P_2$		120.3164	120.3248		

TABLE XXXI. Comparison of theoretical and experimental values for the fine-structure splitting of the $2\,^3P$ level of He-like atoms. $\Delta\nu_{01}$ and $\Delta\nu_{21}$ are the quantities which have to be added to the ionization energy of the $J=1$ level in order to obtain the energies for the $J=0$ and $J=2$ levels, respectively.

	$\Delta\nu_{01}(\text{cm}^{-1})$		$\Delta\nu_{21}(\text{cm}^{-1})$		
Atom	Theory	Expt	Theory	Expt	Ref.
Li II	−5.190	−5.179	−2.085	−2.093	7
Be III	−11.52	• • •	−14.84	−14.8	5
B IV	−15.98	−16.0	−52.40	−52.3	5
C V	−11.7	−13	−134.8	−136	11
N VI	+11.2	+15	−288.0	−305	9
O VII	+65.5	+60	−543.6	−552	10

order expansion used differed from the value listed in the table by only 1 in the last digit quoted. J_{nr} (value adopted), the final value adopted for the given state, is based on the result for the largest expansion used and on the extrapolated value, and is believed to be accurate to within an error of not more than 1 in the last digit quoted. The final values for $E_J - \epsilon_M$ and J_{theor} are also listed. Where no value is given for $E_J - \epsilon_M$ in the table, this correction is assumed to be small enough not to affect the value of J_{theor} to the number of digits given.

In computing the values listed in Tables III–XXII, three auxiliary constants are used for each ion. R_M is used to obtain the ionization energy in cm^{-1} from the eigenvalue of Eq. (1), which is in atomic units of energy; $\alpha^2 R_M$ is used to obtain E_J in units of cm^{-1}; and the constant $2(m/M)R$, where m/M denotes the ratio of the mass of an electron to that of the appropriate nuclear isotope, is used to compute ϵ_M. The values adopted for these three constants in each case are listed in Table XXIII.

IV. COMPARISON WITH EXPERIMENT

In order to facilitate comparison with the experimental values for the energy difference between S and P states, we have listed our final values for J_{theor}, the total theoretical ionization energy in cm^{-1}, in Table XXIV for the singlet states, and in Table XXV for the triplet states. As before, the results listed are estimated to be correct to within 1 or occasionally 2 in the last digit quoted, unless otherwise stated in the table. The error estimates given represent the estimated inaccuracy in the last digit quoted. The entries are followed by the sign ± ? in the cases where we have no completely reliable estimate of the accuracy. They are, however, believed to be accurate to within not more than 2 or 3 in the last digit quoted. (We have quoted results in this category to one less significant digit than the values listed in Tables III–XX.)

The results listed in Table XXV for the triplet P states are for the $J=1$ level. The values of J_{theor} for the $J=0$ and $J=2$ levels may be obtained with the aid of the Table XXVI, which lists the fine-structure splitting for the triplet P states. In this table, $\Delta\nu_{01}$ and $\Delta\nu_{21}$ are the values (correctly signed) which have to be added to J_{theor} for the $J=1$ level to obtain the values of J_{theor} for the $J=0$ and $J=2$ levels, respectively. Thus, for example, in the case of the $2\,^3P$ state of O VII, J_{theor} for $J=1$ has the value $1\,376\,669.28\ \text{cm}^{-1}$, while $\Delta\nu_{01}=65.513$ and $\Delta\nu_{21}=-543.638$. Thus, $J_{\text{theor}}=1\,376\,734.79\ \text{cm}^{-1}$ for the $J=0$ level, and $1\,376\,125.64\ \text{cm}^{-1}$ for the $J=2$ level. The values of $\Delta\nu_{01}$ and $\Delta\nu_{21}$ in Table XXVI include the effect of the α^3 quantum electrodynamic correction, but not the singlet-triplet or higher-order corrections.[28]

A considerable number of accurate measurements of the energy difference between S and P states of two-electron atoms with high values of Z are now available, and they afford an excellent test of the validity of our calculations. We have already made a preliminary comparison between the calculated and observed wavelengths for some of these transitions, and a more complete comparison is made[29] in Tables XXVII–XXX.

In Tables XXVII and XXVIII, we list the transitions from the ground state. λ_{nr} denotes the nonrelativistic value for the wavelength of the given transition, and λ_{theor} the value obtained by including the mass-polarization and relativistic corrections. λ_{tot}, the final theoretical value, includes also the Lamb-shift correction for the ground state.[19] The early but accurate experiments of Robinson[2] have been supplemented by those of Herzberg[6] for He, and by Svensson's accurate remeasurement[12] of some results of Tyrên.[4] The experiments are of high accuracy in all cases, and it will be seen that in most cases the value of λ_{tot} agree with the experimental values to within the estimated uncertainty of the latter. Only for the $1\,^1S$-$3\,^1P$ and $1\,^1S$-$4\,^1P$ transitions in Be III is the discrepancy between theory and experiment substantially larger than the experimental error. The results given in the tables show that the Lamb-shift correction for the $1\,^1S$ state has to be included in order to match the experimental accuracy. They also confirm the value adopted for this correction in the case of He, and show that the correction is at least of the right order of magnitude for the other values of Z.

In Table XXIX, we make a comparison between theory and experiment for the $2\,^1S$-$2\,^1P$ and the $2\,^3S$-$2\,^3P$ transitions. As the energy difference for transitions of the type $n\,^1S$-$n\,^1P$ and $n\,^3S$-$n\,^3P$ is particularly small, the experimental values are subject to only a very small (absolute) error. On the theoretical side, the nonrelativistic energies of the S and P states are almost equal, and largely cancel one another out when computing the energy difference for the transition. Thus, the relativistic, mass-polarization, and Lamb-shift corrections will make a far greater relative contribution to the energy difference than in the case of transitions of the type $m\,^1S$-$n\,^1P$ and $m\,^3S$-$n\,^3P$ for which m is different from n. These points are illustrated excellently by the values listed in Table XXIX. A comparison of λ_{nr} and λ_{theor}, respectively, with the measured value shows the large improvement obtained by including the mass-polarization and relativistic corrections. With the aid of a calculation of Dalgarno,[30] the Lamb-shift correction for the $2\,^1S$ and $2\,^3S$ states of Li^+ has been estimated to have the values -0.69 and -1.14 cm^{-1}, respectively.[21] The value for the $2\,^1S$ state has been used in obtaining the value of λ_{tot} for the second transition listed in the table. No estimates of the Lamb-shift correction for these states are available for higher values of Z. However, one can make a very rough order-of-magnitude estimate of the effect of this correction by utilizing the fact that the most important term behaves as a constant times the fourth power of the atomic number Z. Using the values quoted for Li^+ and scaling up by Z^4, we have made a rough estimate of this correction for other values of Z, and hence we obtained the values of λ_{tot} listed in the table. In all cases except for the $2\,^1S$-$2\,^1P$ transition in Be III, the value of λ_{tot} is far nearer to the experimental result than λ_{theor}. The degree of improvement resulting from the inclusion of so crude an estimate of the Lamb-shift correction may possibly be fortuitous. The results do, however, indicate that an estimate of this correction has to be included before we can match the high experimental accuracy which is currently being achieved for transitions of this type.

In Table XXX, we compare theoretical and experimental wavelengths for some other transitions between S and P states for which accurate experimental results are available. The values quoted for λ_{tot} were obtained by estimating the Lamb-shift correction for the $2\,^1S$ and $2\,^3S$ states through a Z^4 extrapolation as described above. A considerable number of lines in the Li^+ spectrum have been measured by Herzberg and Moore.[7] We have not been able to make an accurate comparison with their results for transitions between triplet states, as our calculations do not include the contribution from the interaction with the nuclear magnetic moment, which gives rise to the hyperfine structure of the triplet levels. (For the Li^7 ion, the hyperfine splitting is of the same order of magnitude as the fine-structure splitting.[7]) The accurate measurements for C V are new ones made by Edlén and Löfstrand.[11] We have also included results which they quote for the $3\,^3S$-$4\,^3P$ and $3\,^3P$-$4\,^3S$ transitions in this atom. These latter measurements were made by Girardeau *et al.*,[11] and they confirm the identification of the line at 756 Å as belonging to the transition $3\,^3P$-$4\,^3S$. The agreement between theory and experiment in Table XXX seems to be satisfactory, except for the $3\,^1S$-$4\,^1P$ line of Li^+.

To summarize, the results listed in Tables XXVII to XXX show our theoretical term values to be in satisfactory agreement with experiment in almost all cases. The results also underline the need for a reliable calculation of the Lamb-shift correction, at least for the $2\,^1S$ and $2\,^3S$ states, in order to obtain term values with an accuracy which matches that of the experimental data currently being achieved.

Our theoretical values listed above for the fine-structure splitting of the $2\,^3P$ states of Li^+ to O VII are compared with the experimental values in Table XXXI. The agreement with experiment may be considered to be satisfactory in view of the fact that the contributions from the singlet-triplet and higher-order quantum electrodynamic corrections have not been included in our calculations.

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Many-Body Calculations for the Heavy Atoms*

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Corrections to the Hartree-Fock (HF) theory which arise as a result of electrostatic configuration interaction are calculated for a heavy ion Pr^{3+}. The effect of configuration interaction upon the $4f^2$ configuration is represented by effective two-body operators of the form $\sum_k a_k C_1^{(k)} C_2^{(k)}$. These operators are evaluated using perturbation theory and graphical methods. The effect of the operators of even rank is to depress the values of the Slater F^k integrals below their HF values. The two-body operators of odd rank do not appear within the ordinary HF theory. The Trees parameter α is the coefficient of an operator of this kind. It is found that the corrections to the Slater integrals converge slowly. The contributions to the operators of odd rank converge properly, however, and we obtain the values $\alpha = 28$, $\beta = -616$, and $\gamma = 1611$. This may be compared with the empirical values $\alpha = 24$, $\beta = -586$, and $\gamma = 728$. The value of γ is determined empirically by the position of a single level, ^1S. It is suggested that the free-ion ^1S level has not been properly identified.

I. INTRODUCTION

The most accurate first-principles calculations of the properties of rare-earth ions have been carried out within the framework of the Hartree-Fock (HF) or self-consistent-field method. Extensive HF calculations have been reported by Freeman and Watson,[1] Froese Fischer,[2] Mann,[3] Clementi and Raimondi,[4] and others. More recently a number of relativistic Hartree-Fock (RHF) calculations have been reported.[5-10]

The optical and magnetic properties of the heavy elements are due mainly to the outer electrons, which are usually quite nonrelativistic. The fact that the RHF calculations of interaction constants of the outer electrons are often significantly more accurate than the nonrelativistic HF calculations may be attributed to differences in the relativistic and nonrelativistic Hamiltonians. For instance, the spin-orbit interaction is contained implicitly in the Dirac Hamiltonian which is used in relativistic self-consistent-field calculations, while it is added as a first-order perturbation to the nonrelativistic HF calculations. This is probably the reason that relativistic calculations of the spin-orbit constant of $5f$ electrons[10] are often considerably more accurate than nonrelativistic calculations. On the other hand, the effects of electrostatic configuration interaction are not included in HF or RHF calculations, and may be expected to give rise to the same kind of discrepancies in both cases. Figure 1 shows the energy levels of Pr^{3+}, which has two $4f$ electrons moving outside a xenon core. There is an obvious correlation between the HF and the experimental levels. However, the energy scale is different in the two cases, and there are a number of crossovers. If instead of using HF values of the integrals we regard them as parameters, we may fit the experimental levels. Table I shows the HF and the empirical values of the Slater integrals. The fact that the HF integrals are much larger than the empirical values corresponds to the fact that the HF energy-level scheme is expanded with respect to what is actually found experimentally. The fit is improved considerably by adding to the Hamiltonian effective operators of odd rank.[11] The qualitative features of these discrepancies may be understood in terms of configuration interaction. The HF calculation assumes that the ground configuration is a pure $4f^2$ configuration, but the $4f$ electrons spend part of their time in higher-lying configurations where they move in large orbits and interact less