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Study of some states of 4—10-electron atoms via the Z expansion

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A perturbation study of a number of states of four- through ten-electron atoms has been made. Second-order energy coefficients for these states are calculated and estimates of the relativistic corrections are also obtained. Higher-order energy coefficients are obtained by a semiempirical fitting of experimental data. Comparisons with experiment are made. The extent of the agreement with experiment is good.

I. INTRODUCTION

In a 1961 paper[1] Sinanoglu observed that the first-order wave function of a many-electron atom is an appropriate linear combination of the first-order wave function of two-electron atoms. This allows the total second-order energy coefficient ϵ_2 to be expressed as a linear combination of two- and three-electron contributions.

In this work, second-order energy coefficients are obtained for all states of four- through ten-electron atoms whose zero-order wave functions can be expressed as $1s^2 2s^a 2p^b$. Estimates of the relativistic corrections are made for each of the states. The effects of degeneracy of the zero-order functions are included for the first- and second-order energy coefficients and for the relativistic corrections. Using these results, semiempirical fits to the observed transition energies are made. Comparisons with experimental results are then made.

II. PERTURBATION EXPANSION

The nonrelativistic Hamiltonian for an N-electron atom of nuclear charge Z in charge-scaled atomic units is

$$H = H_0 + \frac{1}{Z} H_1 , \tag{1}$$

where

$$H_0 = \sum_{I=1}^{N} \left[-\tfrac{1}{2}\nabla_I^2 - \frac{1}{R_I} \right] , \tag{2}$$

$$H_1 = \sum_{J>I}^{N} \frac{1}{R_{IJ}} . \tag{3}$$

The energy through second order is

$$E(Z) = \epsilon_0 Z^2 + \epsilon_1 Z + \epsilon_2 , \tag{4}$$

where

$$\epsilon_1 = (\psi_0 | H_1 | \psi_0) , \tag{5}$$

$$\epsilon_2 = (\psi_0 | H_1 - E_1 | \psi_1) . \tag{6}$$

For the states considered here, ϵ_0 is known exactly as are ψ_0 and ϵ_1 if the state is nondegenerate. For the states considered here that are degenerate, the order of the degeneracy is at most two, and ψ_0 and ϵ_1 are obtained very easily from solutions of 2×2 secular equations.[2]

III. SECOND-ORDER ENERGY COEFFICIENTS

Using as an example the $1s^2 2s\ ^2S$ state of the three-electron atom, we write the first-order wave function as[3]

$$\psi = A \left[a(1,2)2s(3) + \frac{1}{\sqrt{2}} 1s(1)b(2,3) + \frac{1}{\sqrt{2}} 1s(1)c(2,3) + \frac{1}{\sqrt{2}} 1s(2)c(1,3) \right] , \tag{7}$$

where a, b, and c are the first-order wave functions of $1s^2\ ^1S$, $1s2s\ ^1S$, and $1s2s\ ^3S$ states of the two-electron atom. Upon substitution of Eq. (7) into Eq. (6) we obtain

$$\epsilon_2 = \epsilon_2^a + \tfrac{1}{2}\epsilon_2^b + \tfrac{3}{2}\epsilon_2^c + \gamma , \tag{8}$$

where ϵ_2^a, ϵ_2^b, and ϵ_2^c are the second-order coefficients of the two electron $1s^2\ ^1S$, $1s2s\ ^1S$, and $1s2s\ ^3S$ two-electron states, and γ is a linear combination of integrals not given by the pair (or two-electron) coefficients.

The procedure adopted here to evaluate the ϵ_2's of many-electron atoms is first to find estimates for the pair energy coefficients for all the necessary two-electron pairs. Next, three-electron contributions similar to the γ term in Eq. (8) were evaluated. Linear combinations of these coefficients yield a total ϵ_2 for a many-electron state (provided that it is not degenerate).

It should be emphasized that certain of the two-electron pair functions considered, e.g., the $2s^2\,{}^1S$, would appear to present some problems in the usual variational scheme[3] for finding the pair ϵ_2's and first-order two-electron pair function. However, by requiring that the expansion set be orthogonal to the hydrogenlike 1s function, the usual Hylleraas variational expression can be used without modification. Thus we require that the trial ψ_1 for the $2s^2\,{}^1S$ state be chosen such that

$$[\psi_1(1,2)\,|\,1s(2)]=[\psi_1(1,2)\,|\,1s(1)]=0\ , \tag{9}$$

and then we use

$$\epsilon_2=(\psi_1\,|\,H_0-\epsilon_0\,|\,\psi_1)+2(\psi_1\,|\,H_1-\epsilon_1\,|\,\psi_0)\ , \tag{10}$$

where the ϵ_0, ϵ_1, and ψ_0, are those appropriate to the $2s^2\,{}^1S$ state.

Finally, after the variational procedure has been completed, two of the deleted functions, namely,

TABLE I. Pair ϵ_2's in atomic units.[a]

Designation	sum	$-\epsilon_2$
$1s^2$	${}^1S$	0.157 666
$1s\,2s$	${}^1S$	0.114 509
$1s\,2s$	${}^3S$	0.047 409
$1s\,2p$	${}^1P^o$	0.157 028
$1s\,2p$	${}^3P^o$	0.072 999
$2s^2$	${}^1S$	0.036 715
$2s\,2p$	${}^1P^o$	0.095 549
$2s\,2p$	${}^3P^o$	0.028 193
$2p^2$	${}^1S$	0.111 148
$2p^2$	${}^3P$	0.039 363
$2p^2$	${}^1D$	0.086 670
$(2s^2/2p^2)$	${}^1S$	0.016 960

[a] The last entry is the calculated result which is necessary for the degeneracy effect. We define the entry to be

$$(2s^2/2p^2)=\frac{1}{2\sqrt{3}}\left[j(12)\left|\frac{1}{R_{12}}\right|2s(1)2s(2)\right]+\frac{1}{2\sqrt{3}}\left[f(1,2)\left|\frac{1}{R_{12}}\right|2p_0(1)2p_0(2)\right]\ ,$$

where $f(12)$ and $j(12)$ are the first-order wave functions for $2s^2\,{}^1S$ and $2p^2\,{}^1S$, respectively.

TABLE II. Three-electron contributions for ϵ_2 in atomic units.[a]

I	Designation	Sym	$-\gamma$
1	$1s^2 2s$	${}^2S$	0.122 130
2	$1s^2 2p$	${}^2P^o$	0.182 899
3	$2s^2 1s$	${}^2S$	0.093 538
4	$2s^2 2p$	${}^2P^o$	0.062 536
5	$2s\,2p\,1s$	$({}^1p,{}^2p^o)$	0.125 273
6	$2s\,2p\,1s$	$({}^3p,{}^2p^o)$	0.119 754
7	$2s\,2p\,1s$	${}^4P^o$	0.093 109
8	$2p^2 1s$	${}^2S$	0.183 779
9	$2p^2 1s$	${}^2P$	0.162 973
10	$2p^2 1s$	${}^4P$	0.126 186
11	$2p^2 1s$	${}^2D$	0.155 864
12	$2p^2 2s$	${}^2S$	0.057 114
13	$2p^2 2s$	${}^2P$	0.079 501
14	$2p^2 2s$	${}^4P$	0.062 139
15	$2p^2 2s$	${}^2D$	0.063 601
16	$2p^3$	${}^4S$	0.088 013
17	$2p^3$	${}^2P$	0.107 934
18	$2p^3$	${}^2D$	0.099 966
	$(2s^2 1s/2p^2 1s)$	${}^2S$	0.011 905
	$(2s^2 2p/2p^3)$	${}^2P$	0.005 787

[a] The last two entries are the three-electron contributions necessary for the degeneracy effects. The definitions are similar to the last entry in Table I.

TABLE III. Zero-order coefficients and values of λ for degenerate states.[a]

ϕ_0^A	ϕ_0^B	Sym	C_1	C_2	λ
$2s^2$	$2p^2$	^1S	$-0.974\,320$	$0.225\,165$	$-0.195\,845$
$2s^22p$	$2p^3$	$^2P^o$	$-0.986\,327$	$0.164\,797$	$-0.180\,792$
$2s^22p^2$	$2p^4$	^1S	$-0.979\,686$	$0.200\,537$	$-0.295\,811$
$2s^22p^2$	$2p^4$	^3P	$-0.994\,467$	$0.105\,047$	$-0.144\,379$
$2s^22p^2$	$2p^4$	^1D	$-0.994\,467$	$0.105\,047$	$-0.153\,537$
$2s^22p^3$	$2p^5$	$^2P^o$	$-0.991\,349$	$0.131\,249$	$-0.204\,906$
$2s^22p^4$	$2p^6$	^1S	$-0.989\,539$	$0.144\,265$	$-0.321\,232$

[a] We define

$$\psi_0^A = C_1\phi_0^A + C_2\phi_0^B ,$$

$$\psi_0^B = -C_2\phi_0^A + C_1\phi_0^B ,$$

and

$$\psi_1^A = C_1\phi_1^A + C_2\phi_1^B + \lambda\psi_0^B ,$$

$$\psi_1^B = -C_2\phi_1^A + C_1\phi_1^B - \lambda\psi_0^A ,$$

where ϕ_1^A and ϕ_1^B are the first-order wave functions constructed from ϕ_0^A and ϕ_0^B.

the $1s^2$ and $1s2s$ functions are added. This addition assures that no four-electron contributions occur in the expressions of the many-electron ϵ_2's. Similar additions were made for the $2s2p\ ^{1,3}P$ and the $2p^2\ ^1S$ states. For the $2p^2\ ^1S$ state the functions $1s^2$ and $1s2s$ were added. For the $2s2p\ ^{1,3}P$ states, the $1s2p$ function was added. The coefficients of these functions were easily found from elementary perturbation theory and the contributions to the pair energies were found exactly. The entire process was used in order to avoid any four-electron contributions.

Tables I and II list the pair and three-electron coefficients.

IV. DEGENERACY

The most simple many-electron state which is degenerate is the $1s^22s^2\ ^1S$ state of the four-electron atom. We write its zero-order wave function as

$$\psi_0^A = C_1 1s^22s^2 + C_2 1s^22p^2 , \tag{11}$$

where C_1 and C_2 are obtained from the solution of a secular determinant. If we construct a first-order wave function for $1s^22s^2$ and $1s^22p^2$ using the Sinanoglu prescription we obtain

$$\psi_1^A = C_1\phi_1 + C_2\phi_2 , \tag{12}$$

where ϕ_1 and ϕ_2 are the appropriate first-order functions for $1s^22s^2$ and $1s^22p^2$, respectively. Equation (12) is not correct as it stands since using the notation

$$\psi_0^B = -C_2 1s^22s^2 + C_1 1s^22p^2 , \tag{13}$$

$$\psi_1^A = C_1\phi_1 + C_2\phi_2 + \lambda\psi_0^B , \tag{14}$$

is also a solution of the first-order perturbation equation. Using the second-order perturbation equation for ψ_1^A we write

$$(H_0 - \epsilon_0)\psi_2^A + (H_1 - \epsilon_1^A)\psi_1^A - \epsilon_2^A\psi_0^A = 0 . \tag{15}$$

Multiplication of Eq. (15) by ψ_0^B and integration evaluates the unknown coefficient λ. Table III

TABLE IV. Contributions of degeneracy for the first- and second-order perturbation coefficients in atomic units.[a]

Designation	Sym	ϵ_1^D	ϵ_2^D
$2s^2$	^1S	$-0.011\,73$	$0.005\,85$
$2s^22p$	$^2P^o$	$-0.006\,92$	$0.003\,30$
$2s^22p^2$	^1S	$-0.011\,99$	$0.003\,37$
$2s^22p^2$	^3P	$-0.003\,09$	$0.001\,25$
$2s^22p^2$	^1D	$-0.003\,09$	$0.000\,98$
$2s^22p^3$	$^2P^o$	$-0.005\,48$	$0.002\,24$
$2s^22p^4$	^1S	$-0.007\,40$	$-0.000\,51$

[a] The degeneracy coefficients for the companion degenerate states are obtained by changes of sign for both ϵ_1^D and ϵ_2^D. The degeneracy coefficients are defined as $\epsilon_l^D = \epsilon_l - \epsilon_l^*$, where ϵ_l is the perturbation coefficient for the state and ϵ_l^* the perturbation coefficient that would be obtained if the states were nondegenerate.

lists the coefficients C_1, C_2, and λ for each degenerate state in our list. Table IV gives the energy contributions of the degeneracy effects for each pertinent state.

V. RELATIVISTIC CORRECTION

We assume that the relativistic correction is given by

$$\epsilon_{\rm rel}=(\psi\,|\,H_{\rm rel}\,|\,\psi) \tag{16}$$

and that $H_{\rm rel}$ is the Breit Hamiltonian,[4] and that ψ is the nonrelativistic wave function. We introduce some simplifications. The wave function ψ can be expanded as

TABLE V. Pair relativistic coefficients in atomic units.

Designation	Sym	b_1
$1s^2$	^1S	0.480 13
$1s\,2s$	^1S	0.169 47
$1s\,2s$	^3S	0.076 93
$1s\,2p$	$^1P^o$	0.079 78
$1s\,2p$	$^3P^o$	0.065 08
$2s^2$	^1S	0.060 88
$2s\,2p$	$^1P^o$	0.065 44
$2s\,2p$	$^3P^o$	0.042 35
$2p^2$	^1S	0.054 93
$2p^2$	^3P	0.039 10
$2p^2$	^1D	0.045 43

TABLE VI. Transition energies (in cm^{-1}) for some states of the Be isoelectronic sequence.[a]

Z	$2s\,2p\,^1P$	$2p^2\,^1S$	$2p^2\,^3P$[b]	$2p^2\,^1D$
4	42 557	71 820	37 716	56 388
	42 565	71 499	37 716	56 432
5	73 389	128 279	61 588	102 242
	73 396	127 662	61 577	102 362
6	102 358	182 243	85 059	145 913
	102 351	182 520	85 059	145 875
7	130 695	238 267	108 321	188 910
	130 695	235 370	108 325	188 888
8	158 797	287 934	131 516	231 719
	158 798	287 909	131 516	231 722
9	186 885	340 548	154 743	274 582
	186 841	340 424	154 733	274 597
10	214 978	393 308	178 091	317 667
11	243 258	446 377	201 617	361 118
	243 223[c]	446 149[c]	201 589	361 046
12	271 768	499 900	225 409	405 071
	271 687[c]	499 638[c]	225 355	405 100
13	300 581	554 022	249 537	449 662
	300 399[c]	553 673[c]	249 444	449 639
14	329 770	608 885	274 076	495 038
	329 707[c]	608 811[c]	273 912	495 732[c]
15	359 413			541 349
	359 324[c]			541 679[c]
16	389 588			588 753
	389 851[c]			589 689[c]
17	420 369			637 422
	420 698[c]			638 883[c]

[a] For each entry, the first line is the result obtained in the present paper, the second line contains the experimental results of Ref. 7 values otherwise noted.

[b] For the $2p^2\,^3P$ state the term differences are with respect to the $2s\,2p\,^3P^o$ state.

[c] B. C. Fawcett, J. Phys. B 4, 981 (1971).

TABLE VII. Transition energies (in cm^{-1}) for some states of the B isoelectronic sequence.[a]

Z	$2s\,2p^2\,{}^2S$	$2s\,2p^2\,{}^2P$	$2s\,2p^2\,{}^2D$	$2p^3\,{}^4S$ [b]
5	63 775	72 500	47 831	68 222
	63 550	72 532	47 846	68 225
6	97 128	110 465	74 853	99 005
	96 451	110 610	74 890	98 991
7	130 665	145 866	100 926	129 522
	130 887	145 833	100 910	129 519
8	163 955	180 423	126 692	159 891
	164 109	180 385	126 684	159 897
9	197 091	214 692	152 386	190 230
	197 068	214 695	152 130	190 230
10	230 180	248 911	178 133	220 630
	231 710	248 962	178 130	
11	263 331	283 226	204 023	251 183
	262 973[c]	283 668[c]	204 000[c]	251 187[c]
12	296 646	317 739	230 135	281 966
	296 087[c]	317 850[c]	230 088[c]	281 890[c]
13	330 214	352 539	256 542	313 058
	329 397[c]	352 678[c]	256 460[c]	313 984[c]
14	364 124	387 708	283 319	344 544
	362 984[c]	387 998[c]	283 219[c]	344 410[c]
15	398 463	423 330	310 546	
	396 856[c]	423 233[c]	310 500[c]	

[a] For each entry, the first line is the result obtained in the present paper, the second line contains the experimental results of Ref. 7 unless otherwise noted.

[b] For the $2p^3\,{}^4S$ state the term differences are with respect to the $2s\,2p^2\,{}^4P$ state.

[c] B. C. Fawcett, J. Phys. B 4, 981 (1971).

$$\psi=\psi_0+\frac{1}{Z}\psi_1\ , \tag{17}$$

and Eq. (16) can be written as

$$\epsilon_{\mathrm{rel}}=\alpha_2(b_0Z^4+b_1Z^3) \tag{18}$$

since we intend to keep only two terms of the series. Next, we introduce a multiplet averaging of the experimental data. For instance, for the $2s\,2p\,{}^3P$ terms of the four-electron atom, experimental values are given for $J=0$, 1, 2. We replace these three numbers with a single number

$$E(2s\,2p\,{}^3P)=\tfrac{1}{9}E(0)+\tfrac{3}{9}E(1)+\tfrac{5}{9}E(2)\ , \tag{19}$$

where the states are weighted by a $2J+1$ factor. This averaging tends to average out the contributions of the spin-orbit operator and part of the spin-spin operator.

In addition, since we are interested in the contributions in Eq. (18) which are multiplied by Z^3 or Z^4 the retardation terms are ignored as they contribute as Z^2. We finally adopt a simplified formula for a two-electron state as

$$H_{\mathrm{rel}}=\alpha^2\left[-\tfrac{1}{8}\langle P_1^4\rangle-\tfrac{1}{8}\langle P_2^4\rangle+\frac{\pi Z}{2}\langle\delta(\vec{\mathrm{R}}_1)\rangle+\frac{\pi Z}{2}\langle\delta(\vec{\mathrm{R}}_2)\rangle+\pi\langle\delta(\vec{\mathrm{R}}_{12})\rangle\right]\ . \tag{20}$$

Instead of taking ϵ_{rel} as

$$\epsilon_{\mathrm{rel}}=\alpha^2(b_0Z^4+b_1Z^3)\ , \tag{21}$$

we choose to express it as

$$\epsilon_{\mathrm{rel}}=\alpha^2b_0(Z-\eta)^4\ , \tag{22}$$

TABLE VIII. Transition energies of some states of B and C isoelectronic sequences (in cm^{-1}).[a]

Z	$2p^{3}\,{}^{2}P$	$2p^{3}\,{}^{2}D$	$2s^{2}2p^{2}\,{}^{1}S$ [b]	$2s^{2}2p^{2}\,{}^{1}D$
6	168 688	150 417	11 445	10 157
	168 701	150 423	11 454	10 165
7	230 038	202 967	17 377	15 238
	230 291	202 963	17 399	15 229
8	288 930	254 914	22 924	20 072
	288 763	254 911	22 912	20 063
9	347 111	306 735	28 306	24 820
	346 934	306 748	28 302	24 826
10	405 219	358 678	33 605	29 537
			33 606	29 538
11	463 565	410 925	38 861	34 237
	463 639	410 918	38 916	34 094
12	522 347	463 631	44 095	38 933
	522 228[c]	463 633[c]	46 651	39 451
13	581 744	516 947	49 323	43 626
	582 150[c]	516 908[c]	50 631[c]	43 644
14	641 896	571 026	54 556	48 320
	642 285[c]	570 910[c]	54 820[c]	48 508
15		626 025	59 805	53 015
		625 840[c]	60 613[c]	53 435
16			65 075	
			65 604[c]	
17			70 334	
			70 595[c]	

[a] For each entry, the first line is the result obtained in the present paper, the second line contains the experimental results of Ref. 7 unless otherwise noted.

[b] For the $2s^{2}2p^{2}\,{}^{1}S$ state, the term differences are with respect to the $2s^{2}2p^{2}\,{}^{1}D$ state.

[c] B. C. Fawcett, J. Phys. B 4, 981 (1971).

with

$$\eta = -b_1/(4b_0) \, .$$

If the state is nondegenerate, the b_0's can be expressed very easily. Denoting the zero-order wave function as

$$\psi_0 = 1s^2 2s^a 2p^b \, ,$$

$$b_0(1s^2 2s^a 2p_b) = 2b_0(1s) + ab_0(2s) + bb_0(2p) \, , \tag{23}$$

where

$$b_0(1s) = -\tfrac{1}{8} \, ,$$

$$b_0(2s) = -\tfrac{5}{128} \, ,$$

$$b_0(2p) = -\tfrac{7}{384} \, .$$

The b_1's for each of the pairs is given in Table V.

VI. SEMIEMPIRICAL FITS

The experimental energies for a particular state were first multiplet averaged to obtain a single energy for the state with several allowed J values. The theoretical estimates for the nonrelativistic transition energies were calculated through second order

$$T = e_0 Z^2 + e_1 Z + e_2 \, , \tag{24}$$

where the e_i are the differences of the perturbation coefficients between the state and the ground state of the N-electron atom. Similarly, the relativistic estimates were also subtracted. The residue was then assumed to be a polynomial in inverse powers of $\zeta = (Z - s)$:

TABLE IX. Transition energies of some states of C isoelectronic sequences (in cm^{-1}).[a]

Z	$2s\,2p^{3\,3}S$	$2s\,2p^{3\,3}P$	$2s\,2p^{3\,1}D$[b]	$2s\,2p^{3\,3}D$
6	105 305	75 243	87 691	64 053
	105 772	75 227	87 873	64 062
7	154 133	109 175	128 780	92 155
	155 043	109 132	128 873	92 158
8	196 988	142 157	166 770	119 844
	196 434	142 176	166 778	119 833
9	238 039	174 817	203 704	147 452
	237 882	174 827	203 667	147 454
10	278 551	207 407	240 271	175 119
	278 609	204 405	240 270	175 120
11	318 990	240 072	276 784	202 929
	319 325	240 077	276 817	202 923
12	359 579	272 914	313 412	230 963
	360 121[c]	272 914	313 464[c]	230 925
13	400 446	306 023	350 278	259 292
	401 142[c]	306 084	350 303[c]	259 227
14	441 694	339 484	387 483	287 992
	442 517[c]	339 628	387 447[c]	287 854
15	483 409	373 385	425 120	317 142
	484 393[c]	373 763	425 044[c]	317 040
16	525 680		463 282	
	526 162[c]		463 027[c]	
17	568 598		502 063	
	569 595[c]		501 580[c]	

[a] For each entry the first line is the result obtained in the present paper, the second line contains the experimental results of Ref. 7 (unless otherwise noted).

[b] For the $2s\,2p^{3\,1}D$ state, the term differences are with respect to the $2s^2 2p^{2\,1}D$ state.

[c] B. C. Fawcett, J. Phys. B 4, 981 (1971).

$$R=\frac{e_3}{\zeta}+\frac{e_4}{\zeta^2}+\frac{e_5}{\zeta^3}\ . \qquad (25)$$

The screening constant s was arbitrarily chosen to be

$$s=(N-2)/2\ , \qquad (26)$$

where N equals the number of electrons in the state. The first five available members of the isoelectronic series were chosen to obtain the fits. Tables VI–XII show the comparison with experimental data.

Table XIII lists the e_i's for a number of term differences. Table XIV lists the coefficients for obtaining the three-electron contributions of the many-electron ϵ_2's.

VII. CONCLUSIONS

This work is to some extent similar to a previous study of the three-electron atom.[5] Some of the conclusions are the same. (1) It is essential to estimate and to remove the relativistic contributions from the experimental data in order to obtain reasonable fits. (2) The more recent data, particularly those of Fawcett, agrees very well with the predicted values. (3) The Breit Hamiltonian appears to be quite adequate to describe the relativistic contribution for the states considered here. The approximation used here, Eq. (22), seems to be adequate. (4) It is possible to assess the reliability of previous studies. Table XV shows comparisons of the calculated second-order energy coefficients with those

TABLE X. Transition energies for some states of the N isoelectronic sequences (in cm^{-1}).[a]

Z	$2s^22p^3\,{}^2P$ [b]	$2s2p^4\,{}^2S$ [b]	$2s2p^4\,{}^2P$ [b]	$2s2p^4\,{}^4P$
7	9611			88 162
	9614			88 135
8	13 625	168 884	186 554	120 050
	13 652	168 859	185 835	119 933
9	17 468	214 109	232 935	152 060
	17 464	214 166	232 593	152 096
10	21 213	258 408	278 886	184 187
	21 204	258 391	279 025	184 222
11	24 900	302 427	329 682	216 473
	24 900	302 407	329 787	216 469
12	28 549	346 459	370 342	248 975
	28 633	346 461	370 475	248 906
13	32 180	390 680	416 456	281 764
	32 444	390 624	416 341	281 647
14	35 800	435 208	462 684	314 913
	36 419	435 072	462 589	314 782
15	39 421	480 099	509 289	348 501
	40 606	479 035	509 305	348 350
16				

[a] For each entry, the first line is the result obtained in the present paper, the second line contains the experimental results of Ref. 7 (unless otherwise noted).

[b] For the $2s^22p^3\,{}^2P$, $2s2p^4\,{}^2S$, and $2s2p^4\,{}^2P$ states the terms differences are with respect to the $2s^22p^3\,{}^2D$ state.

TABLE XI. Transition energies for some states of the N and O isoelectronic sequences (in cm^{-1}).[a]

Z	$2s2p^4\,{}^2D$ [b]	$2s^22p^4\,{}^1S$ [c]	$2s^22p^4\,{}^1D$	$2s2p^5\,{}^3P$
8	139 179	17 923	15 719	126 276
	139 176	17 924	15 790	126 233
9	176 137	24 020	20 633	165 057
	176 152	24 046	20 709	164 791
10	212 849	29 907	25 624	204 206
	212 853	29 906	25 521	204 269
11	249 558	35 673	30 572	243 575
	249 550	35 662	30 574	243 646
12	286 407	41 364	35 463	283 161
	286 406	41 364	35 475	283 154
13	323 502	47 011	40 304	323 013
	323 644	47 070	40 262	322 914
14	360 932	52 633	45 109	363 200
	361 036	52 780	45 143	363 137
15	398 791	58 389	49 887	403 802
	399 279	58 520	49 661	403 600
16		63 855	54 647	
		64 282	54 475	
17		69 480		
		69 446		

[a] For each entry, the first line is the result obtained in the present paper, the second line contains the experimental results of Ref. 7 (unless otherwise noted).

[b] For the $2s2p^4\,{}^2D$ state, the term differences are with respect to the $2s^22p^3\,{}^2D$ state.

[c] For the $2s^22p^4\,{}^1S$ state the term differences are with respect to the $2s^22p^4\,{}^1D$ state.

TABLE XII. Transition energies and some ionization levels of F and Ne isoelectronic sequences (in cm^{-1}).[a]

Z	$T(2s2p^6\,^2S)$	$IP(2s^22p^5\,^2P)$	$IP(2s^22p^6\,^1S)$
9		140 296	
		140 582	
10	216 455	331 364	174 168
	216 789	331 409	174 193
11	263 965	578 573	381 775
	263 994	578 122	381 983
12	310 792	881 755	647 149
	310 785	881 890	647 106
13	357 673	1 240 703	969 015
	357 661	1 240 789	968 932
14	404 789	1 655 258	1 346 745
	404 800	1 654 957	1 346 800
15	452 306	2 125 316	1 780 205
	452 309	2 124 566	1 780 673
16	500 299	2 650 810	2 269 103
	500 213	2 652 886	2 270 367
17	548 879	3 231 716	2 813 418
	548 867	3 233 966	2 814 533

[a] For each entry the first line is the result obtained in the present paper, the second line contains the experimental results of Ref. 7.

TABLE XIII. Perturbation energy coefficients derived from semiempirical fits for some term differences (in cm^{-1}).[a]

State A	State B	e_3	e_4	e_5
$2s2p\,^1P$	$2s^2\,^1S$	30 811	-32 874	126 539
$2p^2\,^1S$	$2s^2\,^1S$	60 254	-42 700	123 669
$2p^2\,^3P$	$2s2p\,^3P$	23 964	-2 747	-19 665
$2p^2\,^1D$	$2s^2\,^1S$	61 867	-122 914	248 925
$2s2p^2\,^2S$	$2s^22p\,^2P$	37 167	154 816	-462 742
$2s2p^2\,^2P$	$2s^22p\,^2P$	61 773	-177 764	548 068
$2s2p^2\,^2D$	$2s^22p\,^2P$	48 717	-118 739	242 509
$2p^3\,^4S$	$2s2p^2\,^4P$	42 177	-32 558	-14 963
$2p^3\,^2P$	$2s^22p\,^2P$	141 139	-782 515	2 444 888
$2p^3\,^2D$	$2s^22p\,^2P$	100 356	-266 142	545 312
$2s^22p^2\,^1S$	$2s^22p^2\,^1D$	21 714	-51 702	132 031
$2s^22p^2\,^1D$	$2s^22p^2\,^3P$	8 076	-40 616	125 346
$2s2p^3\,^3S$	$2s^22p\,^3P$	144 936	-1 005 668	3 292 622
$2s2p^3\,^3P$	$2s^22p^2\,^3P$	73 876	-199 186	439 669
$2s2p^3\,^1D$	$2s^22p^2\,^1D$	101 332	-411 552	1 351 229
$2s2p^3\,^3D$	$2s^22p^2\,^3D$	63 656	-204 830	366 911
$2s^22p^3\,^2P$	$2s^22p^3\,^2D$	71 903	461 329	-1 093 944
$2s^22p^3\,^2P$	$2s^22p^3\,^4S$	15 755	-7 278	12 079
$2s2p^4\,^2S$	$2s^22p^3\,^2D$	144 045	-718 627	2 325 244
$2s2p^4\,^2P$	$2s^22p^3\,^2D$	175 655	-423 736	722 813
$2s2p^4\,^4P$	$2s^22p^3\,^4S$	74 844	-192 470	161 998
$2s2p^4\,^2P$	$2s^22p^3\,^2D$	105 322	-375 722	872 856
$2s^22p^4\,^1S$	$2s^22p^4\,^1D$	23 452	-71 081	16 802
$2s^22p^4\,^1P$	$2s^22p^4\,^3P$	-16 573	278 310	-764 275
$2s2p^5\,^3P$	$2s^22p^4\,^3P$	101 447	-186 868	-151 128
$2s2p^6\,^2S$	$2s^22p^5\,^2P$	199 874	-1 270 849	-4 006 932

[a] The term differences are $E(A)-E(B)$ and e_i's are defined in Eq. (25).

TABLE XIV. Coefficients for obtaining the total three-electron contributions of the many-electron ϵ_2's.[a]

State	Sym	g_8	g_9	g_{10}	g_{11}	g_{12}	g_{13}	g_{14}	g_{15}	g_{16}	g_{17}	g_{18}
$1s^22s^2$	^1S	0	0	0	0	0	0	0	0	0	0	0
$1s^22s^22p$	^2P	0	0	0	0	0	0	0	0	0	0	0
$1s^22s^22p^2$	^1S	2	0	0	0	2	0	0	0	0	0	0
$1s^22s^22p^2$	^3P	0	$\frac{2}{3}$	$\frac{4}{3}$	0	0	$\frac{2}{3}$	$\frac{4}{3}$	0	0	0	0
$1s^22s^22p^2$	^1D	0	0	0	2	0	0	0	2	0	0	0
$1s^22s^22p^3$	^4S	0	2	4	0	0	2	4	0	1	0	0
$1s^22s^22p^3$	^2P	$\frac{4}{3}$	1	2	$\frac{5}{3}$	$\frac{4}{3}$	1	2	$\frac{5}{3}$	0	1	0
$1s^22s^22p^3$	^2D	0	1	2	3	0	1	2	3	0	0	1
$1s^22s^22p^4$	^1S	$\frac{8}{3}$	2	4	$\frac{10}{3}$	$\frac{8}{3}$	2	4	$\frac{10}{3}$	0	4	0
$1s^22s^22p^4$	^3P	$\frac{2}{3}$	$\frac{8}{3}$	$\frac{16}{3}$	$\frac{10}{3}$	$\frac{2}{3}$	$\frac{8}{3}$	$\frac{16}{3}$	$\frac{10}{3}$	$\frac{4}{3}$	1	$\frac{5}{3}$
$1s^22s^22p^4$	^1D	$\frac{2}{3}$	2	4	$\frac{16}{3}$	$\frac{2}{3}$	2	4	$\frac{16}{3}$	0	1	3
$1s^22s^22p^5$	^2P	$\frac{4}{3}$	4	8	$\frac{20}{3}$	$\frac{4}{3}$	4	8	$\frac{20}{3}$	2	3	5
$1s^22s^22p^6$	^1S	2	6	12	10	2	6	12	10	4	6	10

[a] For each of the states listed here, the zero-order wave function is of the form $1s^22s^22p^b$. The three-electron contributions, $\epsilon_2(3el)$, for these states are

$$\epsilon_2(3el)=2\delta_1+b\delta_2+2\delta_3+b\delta_4$$

$$+b(\delta_5+\delta_6+2\delta_7)+\sum_{I=8}^{18} g_I\delta_I .$$

The g_I's for these states are listed here and the δ_I's are those listed in Table II. Coefficients for the pair contributions are listed in Ref. 8.

TABLE XV. A comparison of the calculated ϵ_2's with the results of Scherr, Silverman, and Matsen in atomic units.

N	Results of Scherr *et al.*	Present results
3	−0.4089	−0.408 16
4	−0.880	−0.876 60
5	−1.843	−1.833 91
6	−3.253	−3.242 80
7	−5.20	−5.190 97
8	−8.05	−7.975 34
9	−11.64	−11.515 66
10	−16.07	−15.899 96

of Scherr, Silverman, and Matsen.[6] In this case, the agreement is very good.

For the states considered here we conclude that the calculations of the ϵ_2's are quite straightforward if the state is nondegenerate. The major problem of dealing with larger atomic systems appears to find a simple way of dealing with this problem. Extensions to excited states of 4–10 electron systems should prove to be relatively simple. Calculations of one-electron operators, for example, transition probabilities, are possible for the states considered here and for two- and three-electron atoms.

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