SOME FIRST-ORDER PERTURBATION ENERGY VALUES*

by

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In the conventional perturbation study of the two-electron atom the perturbation is chosen to be the electron-electron interaction term in the potential energy[1]:

$$H = H_0 + Z^{-1}r_{12}^{-1}$$

where H_0 is the zero-order Hamiltonian with eigenfunctions Ψ_{0p}, say, and Z is the nuclear charge. Then, as is well known, the first-order perturbation energy correction is given by

$$\epsilon_1(p) = \int d\tau\ \Psi_{0p}^*\Psi_{0p}/Zr_{12}.$$

In this note, the $\epsilon_1(p)$ are computed for a number of the singly-excited singlet and triplet S, P, and D symmetry states of the helium iso-electronic sequence. By a singly-excited state is meant one whose correct zero-order wavefunction is of the form of a properly symmetrized product $\Psi_{0p} = \Psi_{100}(1)\Psi_{n\ell m}(2)$ where the $\Psi_{n\ell m}$ are the hydrogen problem eigenfunctions. These ϵ_1 values are needed for the calculation of the higher-order energy coefficients.

In the standard spectroscopic notation for $\Psi_{n\ell m}$,

$$\epsilon_1 = [1s1s|n\ell n\ell] \pm [1sn\ell|1sn\ell],$$

where, for example, the first integral is the coulomb energy of interaction between the charge distribution 1s1s and $n\ell n\ell$.

In terms of the hypergeometric function

$$F(a,b|c|z) = \sum_{n=0}^{\infty} \frac{(a)_n (b)_n}{(c)_n\, n!}\, z^n,$$

$$a_n = \Gamma(a+n)/\Gamma(a),$$

it follows that

$$[1s1s|n\ell n\ell] = Zn^{-2}\left\{1 + \frac{(n+\ell)!\, n^{2n-2\ell-2}}{(2\ell+1)!\,(n-\ell-1)!\,(n+1)^{2n+1}}\left[F(1+\ell-n, 2+\ell-n|2\ell+2|n^{-2}) - \frac{(n^2+n+1)}{(n-\ell-1)(n+1)} F(1+\ell-n, 1+\ell-n|2\ell+2|n^{-2})\right]\right\}$$

and

$$[1sn\ell|1sn\ell] = \frac{4Zn(n+\ell)!}{[(2\ell+1)!]^2 (2\ell+1)(n-\ell-1)!\,(n+1)^{2\ell+5}} \sum_{r=0}^{\infty} \frac{(1+\ell-n)_r (r+1)}{(2\ell+2)_r} \left(\frac{2}{n+1}\right)^r \times \sum_{s=0}^{r+1} \frac{(2\ell+2+s)!}{2^s\, s!} F(\ell+1-n, 2\ell+3+s|2\ell+2|\tfrac{1}{n+1})\Big\}$$

These integrals are presented in Table I.

The ϵ_1 values for the singlet and triplet NS, NP and ND states of the helium isoelectronic series ($N < 20$) are presented in Tables II-IV. The calculations were performed in double precision (27 significant decimal figures) on the CDC 1604 located on this campus. Pilot calculations indicate an accuracy of at least 24 figures, and the data have been rounded accordingly.

[1] In order to obtain this form of the hamiltonian, atomic units of length Za_0 and of energy $2RhcZ^2$ are used. However, in the discussion that follows and in the tables, units of a_0 and $2Rhc$ respectively are used.

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TA[redacted]ectron Interaction Integrals in Atomic Units

N	[1S1S/NSNS] /Z	[1SNS/1SNS] /Z
2	2.09876543209876543209876 5E-01	2.19478737997256515775034 2E-02
3	9.94873046875000000000000E-02	5.76782226562500000000000E-03
4	5.76332800000000000000000E-02	2.33963519999999999999999E-03
5	3.75168590122186658537824 5E-02	1.17682873369292169779900 3E-03
6	2.63434598029044972202509 8E-02	6.74576708335991811589008 8E-04
7	1.95059335632095098844729 4E-02	4.22387915683941628230968 5E-04
8	1.50210161996429811910284 1E-02	2.81924362293886868176400 2E-04
9	1.19216931224101390000000 0E-02	1.97505330644584439999999 8E-04
10	9.69102427497453432004435 3E-03	1.43722125568717367005611 1E-04
11	8.03238585129568037561664 7E-03	1.07836852056776469371711 9E-04
12	6.76572184559716260538215 3E-03	8.29778242034861309777428 2E-05
13	5.77661147027951732169509 E-03	6.52129673291952208988260 2E-05
14	4.98952387355334052090490 1E-03	5.21805787732304535615408 6E-05
15	4.35297310861408081122255 1E-03	4.24033997589731578804359 5E-05
16	3.83088608059747361900343 3E-03	3.49249435659994269531609 6E-05
17	3.39738046407805803027700 7E-03	2.91072222783122613846424 8E-05
18	3.03349582910086426823006 9E-03	2.45135328281859090212584 6E-05
19	2.72508564588154446581840 5E-03	2.08380756104377127367104 7E-05
20	2.46142188167420114992188 5E-03	1.78623579348118826655936 1E-05

N	[1S1S/NPNP] /Z	[1SNP/1SNP] /Z
2	2.42798353909465020576131 7E-01	1.70705685108977290047248 9E-02
3	1.08825683593750000000000 0E-01	4.53186035156250000000000 0E-03
4	6.15162880000000000000000 0E-02	1.84418304000000000000000 0E-03
5	3.94919301660485359616589 6E-02	9.28945020211295536308096 5E-04
6	2.74824023469190390613337 0E-02	5.32892432188914360929421 1E-04
7	2.02216470970881800894858 3E-02	3.33824060964715840782446 2E-04
8	1.54998300360311553017824 3E-02	2.22877622797329173010633 7E-04
9	1.22576634096194872000000 0E-02	1.56170821697013600000000 0E-04
10	9.93578221793851124929065 6E-03	1.13659808051873426909475 8E-04
11	8.21618487835634368960899 4E-03	8.52896687977077962004693 6E-05
12	6.90724051068981047047453 1E-03	6.56335897930627579967707 1E-05
13	5.88788708540589057832698 5E-03	5.15852095153811076501177 1E-05
14	5.07859663406743705921731 9E-03	4.12782834931489514893000 6E-05
15	4.42537897542150055268886 1E-03	3.35452280828262375189756 2E-05
16	3.89053751852820955980009 7E-03	2.76299412711035539358775 9E-05
17	3.44710592996325602262792 7E-03	2.30280283741185037625561 7E-05
18	3.07538114810727260101130 8E-03	1.93941940644334683331635 0E-05
19	2.76069625301717885222736 7E-03	1.64866251897730469222717 3E-05
20	2.49195117582029165066408 7E-03	1.41325342708788889470696 0E-05

TABLE I. Continued

N	[1S1S/NDNC] /Z	[1SND/1SND] /Z
3	1.110229492187500000000000E-01	2.471923828125000000000000E-04
4	6.245017600000000000000000E-02	1.318584320000000000000000E-04
5	3.997153714499822181578011E-02	7.341110654804578495072831E-05
6	2.776038433772337620692570E-02	4.424851106405615903871695E-05
7	2.039638130584072998317424E-02	2.851689447815886069292901E-05
8	1.561727735122057729961021E-02	1.938273451465877879803398E-05
9	1.234018245635709040000000E-02	1.374576762479011200000001E-05
10	9.995955149323494311687540E-03	1.008929042069964351783517E-05
11	8.261402824972751094603408E-03	7.618162753599473045534251E-06
12	6.942075165212680036381447E-03	5.890050409762642926303856E-06
13	5.915288728730418172120338E-03	4.646162425873358511605765E-06
14	5.100537977912009114469100E-03	3.728546906562507276037555E-06
15	4.443219444614686444459242E-03	3.037045285275432557929287E-06
16	3.905238516610295941495060E-03	2.506217312123009302173383E-06
17	3.459362871371720056865816E-03	2.092050328456574608710269E-06
18	3.085707094256108967058436E-03	1.764221244421282263896754E-06
19	2.769476408418814786285643E-03	1.501382230564176059753297E-06
20	2.499479292690519923496315E-03	1.288211828203079740686713E-06

TABLE II. The ϵ_1 in Atomic Units. S-States

N	$\epsilon_1(N^1S)$	$\epsilon_1(N^3S)$
2	2.318244170096021947873800E-01	1.879236694101508916323731E-01
3	1.052551269531250000000000E-01	9.371948242187500000000000E-02
4	5.997291520000000000000000E-02	5.529364480000000000000000E-02
5	3.869368774591158755158146E-02	3.634003027852574415598345E-02
6	2.701803651124048903183999E-02	2.566888309456850540866197E-02
7	1.992832147889345151270390E-02	1.908354564752556825624197E-02
8	1.530294056193686805920481E-02	1.473909183734909432285201E-02
9	1.211919845305472344000000E-02	1.172418779176555456000000E-02
10	9.834746400543251687049965E-03	9.547302149405816953038742E-03
11	8.140222703352456844988359E-03	7.924548999238903906244936E-03
12	6.848699669800648736359896E-03	6.682744021393676474404410E-03
13	5.841824437608712453068335E-03	5.711398502950322011270684E-03
14	5.041704452326570974466442E-03	4.937343294780110067343360E-03
15	4.395376508376053969102987E-03	4.310569708855107653342114E-03
16	3.865811024163473045956594E-03	3.795961137031474192050272E-03
17	3.426487686356370291661650E-03	3.368273241799745768892365E-03
18	3.058009361929050177251328E-03	3.008982296272678359208811E-03
19	2.745923721491982178555116E-03	2.704247570271106753081695E-03
20	2.479284239609013032587478E-03	2.443559523739389267256291E-03

TABLE III. The ϵ_1 in Atomic Units. P-States

N	$\epsilon_1(N^1P)$	$\epsilon_1(N^3P)$
2	2.59868922420362749580856 6E-01	2.25727785398567291571406 8E-01
3	1.13357543945312500000000E-01	1.04293823242187500000000E-01
4	6.33604710400000000000000E-02	5.96721049600000000000000E-02
5	4.04208751862598314979670 6E-02	3.85629851458372404253508 6E-02
6	2.80152947791079534222631 2E-02	2.69495099147301247004042 8E-02
7	2.05554711580528959302682 8E-02	1.98878230361234642487033 9E-02
8	1.57227076588284844747930 6E-02	1.52769524132338261287718 0E-02
9	1.24138342313165008000000 0E-02	1.21014925879224736000000 0E-02
10	1.00494420259903846762001 3E-02	9.82212240988663782238118 1E-03
11	8.30147454715405148580946 3E-03	8.13089520955863589340852 4E-03
12	6.97287410048287322847130 2E-03	6.84160692089674771247776 0E-03
13	5.93947229492127168597710 2E-03	5.83630187589050947067686 7E-03
14	5.11987491756058601070661 9E-03	5.03731835057428810772801 9E-03
15	4.45892420350432679020783 6E-03	4.39183374733867431516988 5E-03
16	3.91816745979931311373597 5E-03	3.86290757725710600586422 0E-03
17	3.47013395833737452639048 3E-03	3.42407790158913751886537 0E-03
18	3.09477534217170606934447 1E-03	3.05598695404283913267814 4E-03
19	2.77718287820695189914963 9E-03	2.74420962782740580530509 5E-03
20	2.50608371009117053961115 7E-03	2.47781864154941276171701 8E-03

TABLE IV. The ϵ_1 in Atomic Units. D-States

N	$\epsilon_1(N^1D)$	$\epsilon_1(N^3D)$
3	1.11270141601562500000000 0E-01	1.10775756835937500000000 0E-01
4	6.25820344320000000000000 0E-02	6.23183175680000000000000 0E-02
5	4.00449482515462676007308 4E-02	3.98981260384501760308293 9E-02
6	2.78046328487874323659644 1E-02	2.77161358266593200478869 8E-02
7	2.04253782003188888438671 7E-02	2.03683444113625711224813 1E-02
8	1.56366600857352360784082 4E-02	1.55978946167059185208121 8E-02
9	1.23539282239818805120000 0E-02	1.23264366887323002880000 0E-02
10	1.00060444397441939552053 7E-02	9.98586585890279466816970 5E-03
11	8.26902098772635056764894 2E-03	8.25378466221915162155787 3E-03
12	6.94796521562244267930775 1E-03	6.93618511480291739345514 4E-03
13	5.91993491115629153063194 4E-03	5.91064254630454481360873 3E-03
14	5.10426652481857162174513 7E-03	5.09680943100544660719306 2E-03
15	4.44625648989961877017172 E-03	4.44018239932941101190131 3E-03
16	3.90774473392241895079723 3E-03	3.90273229929817293219288 7E-03
17	3.46145492170017663147452 7E-03	3.45727082104326348225710 6E-03
18	3.08747131550053024932233 3E-03	3.08394287301168768479453 9E-03
19	2.77097779064937896234539 7E-03	2.76797502618825061022589 0E-03
20	2.50076750451872300323700 2E-03	2.49819108086231684375562 8E-03