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Correlation Energies of Some States of 3-10 Electron Atoms

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The nonrelativistic eigenvalues of several states of 3–10 electron atoms are calculated to second order in the nuclear charge Z. It is noted that with some modifications the Hylleraas variational procedure can be employed successfully for a many-electron atom.

I. INTRODUCTION

Conventional Schrödinger perturbation theory presents the energy and wave function of an atomic state, of arbitrary nuclear charge Z, as an expansion in the inverse powers of the nuclear charge. For any atomic state the zero-order wave function Ψ_0 and the first two perturbation coefficients ϵ_0 and ϵ_1 can be found exactly. The second-order coefficient ϵ_2 has been calculated for a number of atomic states using a variational perturbation technique due to Hylleraas.[1] Most of these calculations have been restricted to two-electron systems.[2] In order to extend the procedure to a many-electron atom, Chisholm and Dalgarno[3] have shown that the first-order wave function for a many-electron atom is naturally partitioned into two-electron pair functions. The purpose of this work is to show that the calculation of the first-order wave functions and second-order perturbation coefficients is practical for many-electron atoms.

II. METHODS

The general procedure is to choose Z(a.u.) as a scale of distance, and Z^2(a.u.) as the scale of energy. Then for an N-electron atom of nuclear charge Z,

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

$$H_0 = \sum_{i=1}^{N} \left(-\frac{1}{2} \nabla_i 2 - \frac{1}{r_i} \right) , \tag{2}$$

and $$H_1 = \sum_{i<j} \frac{1}{r_{i,j}} . \tag{3}$$

Then to second order, the energy is given by

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

where $$\epsilon_1 = (\Psi_0 | H_1 | \Psi_0) , \tag{5}$$

$$\epsilon_2 = (\Psi_0 | H_1 - \epsilon_1 | \Psi_1) , \tag{6}$$

and Ψ_0 and Ψ_1 are solutions of

$$(H_0 - \epsilon_0)\Psi_0 = 0 , \tag{7}$$

$$(H_0 - \epsilon_0)\Psi_1 + (H_1 - \epsilon_1)\Psi_0 = 0 . \tag{8}$$

The function Ψ_0 is simply a product of scaled hydrogen-atom solutions and can be easily obtained for atomic states. The perturbation coefficients ϵ_0 and ϵ_1 are also easily obtained. The motivation in this work is to show that the calculation of the second-order coefficient is feasible for many-electron atoms.

The first-order wave function for an N-electron atom can be written as a linear combination of two-electron, first-order wave functions multiplied $(N-2)$ hydrogen-atom solutions. As an example, if we consider the $1s^2 2s\, {}^2S$ state of the three-electron atom, it is relatively easy to show that

$$\Psi_1 = \sqrt{\tfrac{1}{2}}(1 - P_{13})[a(1,2)2s(3) + \sqrt{\tfrac{1}{2}}c(1,3)1s(2) + \sqrt{\tfrac{1}{2}}\, 1s(1)c(2,3) + \sqrt{\tfrac{1}{2}}\, 1s(1)b(2,3)] , \tag{9}$$

where P_{13} is permutation operator, and Ψ_1 is a solution of

$$(-\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \tfrac{1}{2}\nabla_3^2 - 1/r_1 - 1/r_2 - 1/r_3 - \epsilon_0)\Psi_1(1,2,3) + [1/r_{12} + 1/r_{13} + 1/r_{23} - \epsilon_1(1s^2 2s\, {}^2S)]1s(1)1s(2)2s(3) = 0, \tag{10}$$

where $\epsilon_0 = -\frac{9}{8}$ and provided that $a(1,2)$, $b(1,2)$, and $c(1,2)$ are solutions of the first-order perturbation equations for the $1s^2\, 1S$, $1s2s\, {}^1S$, and $1s2s\, {}^3S$ states, respectively; namely,

$$(-\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - 1/r_1 - 1/r_2 - \epsilon_0^A)a(1,2) + (1/r_{12} - \epsilon_1^A)1s(1)1s(2) = 0 , \tag{11}$$

$$(-\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - 1/r_1 - 1/r_2 - \epsilon_0^B)b(1,2) + (1/r_{12} - \epsilon_1^B)\sqrt{\tfrac{1}{2}}[1s(1)2s(2) + 2s(1)1s(2)] = 0 , \tag{12}$$

$$(-\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - 1/r_1 - 1/r_2 - \epsilon_0^C)c(1,2) + (1/r_{12} - \epsilon_1^C)\tfrac{1}{2}[1s(1)2s(2) - 2s(1)1s(2)] = 0 , \tag{13}$$

where $\epsilon_0^A = -1$, $\epsilon_0^B = -\frac{5}{8}$, $\epsilon_1^A = \frac{5}{8}$, $\epsilon_1^B = \frac{169}{729}$, $\epsilon_1^C = \frac{137}{729}$.

Similar expressions can be written for any atomic state. Chisholm and Dalgarno[3] have shown that, upon substitution of the expression for Ψ_1 [Eq. (9)] into the defining equation for ϵ_2 [Eq. (6)], one obtains

$$\epsilon_2(1s^2 2s\, {}^2S) = \epsilon_2^A + \tfrac{1}{2}\epsilon_2^B + \tfrac{3}{2}\epsilon_2^C + \delta , \tag{14}$$

where ϵ_2^A, ϵ_2^B, and ϵ_2^C are the second-order coefficients for the $1s^2\, {}^1S$, $1s2s\, {}^1S$, and $1s2s\, {}^3S$ states, respectively, and δ is a contribution arising from three-electron integrals that occur in the evaluation. Expressions similar to Eq. (14) can readily be found for all atomic states. In all cases, there occur a linear combination of two-electron contributions similar to the first three terms of Eq. (14), which we will call pair energies. In addition, three-electron terms occur similar to the δ term in Eq. (14). Lastly, a few four-electron contributions occur which were handled by modifying the definitions of two of the two-electron contributions for the states considered in this work. In particular we defined

$$\epsilon_2^F = \bar{\lambda}_2^F + [a(1,2)|2s(1)2s(2)][1s(1)1s(2)|1/r_{12}|2s(1)2s(2)] , \tag{15}$$

and $$\epsilon_2^J = \lambda_2^J + 3[a(1,2)|2p(1)2p(2)][1s(1)1s(2)|1/r_{12}|2p(1)2p(2)] , \tag{16}$$

where $\bar{\lambda}_2^F$ and λ_2^J are the pair energies arising from $2s^2\,{}^1S$ and $2p^2\,{}^1P$ states.

By making this modification in the definitions, it is possible to divide the second-order perturbation coefficient of a state into two- and three-electron contributions.

The procedure adopted here is to evaluate the two- and three-electron clusters, and finally to take proper linear combinations to form the total two- and three-electron contributions for a given state. No difficulty is encountered from excited states and recalculation for more complicated states is unnecessary. For instance, to extend the calculation to the ground state of an 11-electron atom many of the required parts are already available from the calculation of the 10-electron atom.

III. THE PAIR CONTRIBUTIONS

Table I presents the coefficients of the pair energies for some of the states being considered here. Thus the pairs contribution to the $1s^2 2s^2 2p\,{}^2P$ state of the five-electron atom is

$$\epsilon^1 = \epsilon_2^A + \epsilon_2^B + 3\epsilon_2^C + \tfrac{1}{2}\epsilon_2^D + \tfrac{3}{2}\epsilon_2^E + \epsilon_2^F + \tfrac{1}{2}\epsilon_2^G + \tfrac{3}{2}\epsilon_2^H . \tag{17}$$

Table II presents the calculated pair energies for each state; the two electron contribution is easily obtained by adding the terms with the indicated coefficients. The sums are listed in Table III.

The calculations for states involving, at most, one promoted electron have previously been reported.[4–7] All of these calculations use the variational-perturbation procedure of Hylleraas. In order to use this procedure for doubly promoted states, such as $2s^2\,{}^1S$, a modification of the standard Hylleraas procedure is necessary. The variational expression for ϵ_2 is

$$\epsilon_2 = (\Psi_1|H_0 - \epsilon_0|\Psi_1) + 2(\Psi_1|H_1 - \epsilon_1|\Psi_0) , \tag{18}$$

which was used without modification for the $1s^2\,{}^1S$, $1s2s\,{}^3S$, $1s2p\,{}^1P$, $1s2p\,{}^3P$, and $2p^2\,{}^3P$ states. Here Ψ_1 and Ψ_0 are both two-electron wave functions. For the $1s2s\,{}^1S$ state, the procedure is identical except that the zero-order wave function $1s^2\,{}^1S$ is included in the expression for $\Psi_1(1s2s\,{}^1S)$. This is sufficient to insure that the calculated ϵ_2 for this state is an upper bound. For the $2s^2\,{}^1S$, $2p^2\,{}^1S$, $2s2p\,{}^1P$, $2s2p\,{}^3P$, and $2p^2\,{}^1D$ states use was made of Eq. (18) except that a four-electron expression was made for Ψ_1 and Ψ_0. The Ψ_1 corresponding to, say, the $1s^2 2s^2\,{}^1S$ state was written in a manner similar to Eq. (9). Upon substitution of this expression into Eq. (18), and assuming that the other pair functions satisfy the first-order perturbation equations, variational expression is readily found for the pair function corresponding to $2s^2\,{}^1S$. Similar expressions

TABLE I. Coefficients of total pair contributions in terms of pair energies.

State	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*J*	*K*	*L*
$1s^2 2s\,{}^2S$	1	1/2	3/2	···	···	···	···	···	···	···	···
$1s^2 2p\,{}^2P$	1	···	···	1/2	3/2	···	···	···	···	···	···
$1s^2 2s^2\,{}^1S$	1	1	3	···	···	1	···	···	···	···	···
$1s^2 2s^2 2p\,{}^2P$	1	1	3	1/2	3/2	1	1/2	3/2	···	···	···
$1s^2 2s^2 2p^2\,{}^1S$	1	1	3	1	3	1	1	3	1	···	···
$1s^2 2s^2 2p^2\,{}^3P$	1	1	3	1	3	1	1	3	···	1	···
$1s^2 2s^2 2p^2\,{}^1D$	1	1	3	1	3	1	1	3	···	···	1
$1s^2 2s^2 2p^3\,{}^4S$	1	1	3	3/2	9/2	1	3/2	9/2	···	3	···
$1s^2 2s^2 2p^3\,{}^2P$	1	1	3	3/2	9/2	1	3/2	9/2	2/3	3/2	5/6
$1s^2 2s^2 2p^3\,{}^2P$	1	1	3	3/2	9/2	1	3/2	9/2	···	3/2	3/2
$1s^2 2s^2 2p^4\,{}^1S$	1	1	3	2	6	1	2	6	4/3	3	5/3
$1s^2 2s^2 2p^4\,{}^3P$	1	1	3	2	6	1	2	6	1/3	4	5/3
$1s^2 2s^2 2p^4\,{}^1D$	1	1	3	2	6	1	2	6	1/3	3	8/3
$1s^2 2s^2 2p^5\,{}^2P$	1	1	3	5/2	15/2	1	5/2	15/2	2/3	6	10/3
$1s^2 2s^2 2p^6\,{}^1S$	1	1	3	3	9	1	3	9	1	9	5

TABLE II. Calculated pair energies.

State	Designation	ϵ_2	No. of terms in the expansion
$1s^2\,{}^1S$	a	$-0.157\,666\,40$	100
$1s2s\,{}^1S$	b	$-0.114\,509\,48$	132
$1s2s\,{}^3P$	c	$-0.047\,409\,29$	132
$1s2p\,{}^1P$	d	$-0.157\,028\,49$	160
$1s2p\,{}^3P$	e	$-0.072\,998\,90$	160
$2s^2\,{}^1S$	f	$-0.037\,879\,77$	138
$2s2p\,{}^1P$	g	$-0.094\,116\,62$	160
$2s2p\,{}^3P$	h	$-0.041\,793\,72$	160
$2p^2\,{}^1S$	j	$-0.117\,552\,70$	138
$2p^2\,{}^3P$	k	$-0.039\,394\,11$	142
$2p^2\,{}^1D$	l	$-0.084\,829\,87$	110

were found for the other pair functions arising from doubly promoted zero-order wave functions.

The calculation of the pair energies and pair function is quite simple. The extension to systems containing more electrons and to excited states is quite feasible.

In most cases for the doubly promoted pair functions an expression in terms of Legendre polynomials was employed. This obviously might be improved by introduction of the inter-electron coordinate r_{12}. However, some work in this direction indicated only a slight improvement was obtained.

Some comment is necessary to explain the particular choice of number of terms in the expansions for the pair functions. The choices are somewhat arbitrary. A restraint is imposed by the size of the available storage. The basis set was truncated by adopting a convenient total upper limit to the metric of the basis set. If the expansion is written as

$$\Psi_1 = \sum_{a,b,c} (r_1^a r_2^b + r_1^b r_2^a) \times r_{12}^c e^{-\frac{1}{2}k(r_1+r_{12})} C(a,b,c)\,, \qquad (19)$$

then we define $g = a + b + c$ as the metric. The number of terms in the expansion was taken by simply including all appropriate terms corresponding to choices of a, b, and c whose sum is less than, or equal to, some maximum metric.

We would like to emphasize that the calculation of the pair functions considered here gives approximate first-order wave functions for all the states listed in Tables III and IV. In all cases the pair energies listed in Table II are upper bounds.

TABLE III. First- and second-order perturbation coefficients for some atomic states.

State	Designation	ϵ_1	$-\epsilon_2$ Pair contribution	$-\epsilon_2$ 3-electron contribution	Total
$1s^22s$	^2S	1.022 805	0.286 035	0.122 130	0.408 165
$1s^22p$	^2P	1.093 526	0.345 678	0.182 900	0.528 579
$1s^22s^2$	^1S	1.559 274	0.452 283	0.429 661	0.881 945
$1s^22s2p$	$^1P^\circ$	1.682 737	0.568 164	0.541 609	1.109 773
$1s^22s2p$	$^3P^\circ$	1.624 143	0.515 841	0.508 162	1.024 003
$1s^22p^2$	^1S	1.790 575	0.651 244	0.722 225	1.373 469
$1s^22p^2$	^3P	1.726 114	0.573 085	0.642 658	1.215 744
$1s^22p^2$	^1D	1.747 208	0.618 521	0.677 529	1.296 050
$1s^22s2p^2$	$^2P^\circ$	2.327 526	0.750 044	1.106 606	1.856 650
$1s^22s2p^2$	^2S	2.471 576	0.889 361	1.357 747	2.247 109
$1s^22s2p^2$	^2P	2.477 435	0.863 526	1.333 142	2.196 668
$1s^22s2p^2$	^4P	2.389 544	0.785 041	1.234 887	2.019 928
$1s^22s2p^2$	^2D	2.439 935	0.856 639	1.295 898	2.152 537
$1s^22p^3$	$^4S^\circ$	2.522 765	0.839 886	1.467 289	2.307 175
$1s^22p^3$	$^2P^\circ$	2.582 422	0.929 855	1.576 722	2.506 578
$1s^22p^3$	$^2D^\circ$	2.554 406	0.908 040	1.537 429	2.445 547
$1s^22s^22p^2$	^1S	3.302 700	1.165 359	2.275 179	3.440 538
$1s^22s^22p^2$	^3P	3.258 864	1.087 200	2.200 801	3.288 002
$1s^22s^22p^2$	^1D	3.279 958	1.132 636	2.227 489	3.360 125
$1s^22s^22p^3$	^3S	3.436 196	1.198 282	2.509 272	3.707 554
$1s^22s2p^3$	^5S	3.319 008	1.093 636	2.110 798	3.204 435
$1s^22s2p^3$	^1P	3.459 633	1.262 089	2.657 268	3.919 357
$1s^22s2p^3$	^3P	3.401 039	1.209 766	2.547 081	3.756 848
$1s^22s2p^3$	^1D	3.438 539	1.240 247	2.574 859	3.814 107
$1s^22s2p^3$	^3D	3.379 946	1.187 951	2.491 536	3.679 488

TABLE IV. First- and second-order energy coefficients for some atomic states.

State	Designation	ϵ_1	$-\epsilon_2$ Pair contribution	 3-electron contribution	Total
$1s^22p^4$	^1S	3.600 942	1.326 019	3.006 988	4.333 007
$1s^22p^4$	^3P	3.539 308	1.247 860	2.890 945	4.138 806
$1s^22p^4$	^1D	3.560 402	1.293 296	2.954 858	4.248 154
$1s^22s^22p^3$	$^4S^\circ$	4.353 532	1.463 750	3.800 262	5.264 012
$1s^22s^22p^3$	$^2P^\circ$	4.400 781	1.553 719	3.928 406	5.482 125
$1s^22s^22p^3$	$^2D^\circ$	4.385 173	1.531 903	3.859 368	5.391 272
$1s^22s2p^4$	^2S	4.576 597	1.673 885	4.423 811	6.097 696
$1s^22s2p^4$	^2P	4.582 456	1.648 049	4.409 235	6.097 285
$1s^22s2p^4$	^4P	4.494 566	1.569 565	4.257 193	5.826 759
$1s^22s2p^4$	^2D	4.544 956	1.641 162	4.368 782	6.009 945
$1s^22p^5$	$^2P^\circ$	4.719 209	1.695 228	4.922 845	6.618 074
$1s^22s^22p^4$	^1S	5.707 238	1.059 631	6.248 681	8.308 313
$1s^22s^22p^4$	^3P	5.661 902	1.981 473	6.150 391	8.131 865
$1s^22s^22p^4$	^1D	5.682 996	2.026 909	6.173 479	8.200 388
$1s^22s2p^5$	$^1P^\circ$	5.892 779	2.137 211	6.920 389	9.057 601
$1s^22s2p^5$	$^3P^\circ$	5.834 185	2.084 889	6.792 546	8.887 435
$1s^22p^6$	^1S	6.062 695	2.181 991	7.637 846	9.819 837
$1s^22s^22p^5$	$^2P^\circ$	7.134 334	2.538 590	9.216 515	11.755 106
$1s^22s2p^6$	^2S	7.337 868	2.639 606	10.103 879	12.743 486
$1s^22s^22p^6$	^1S	8.770 829	3.135 191	13.138 776	16.272 878

IV. THE THREE-ELECTRON CONTRIBUTIONS

The evaluations of the three-electron contributions is complicated by the large number of required integrals. The complexity of the algebra can be reduced somewhat by a division into three-electron clusters. An example of a required integral is

$$A_1 = [a(1,2)2p(3)\left|\frac{1}{r_{13}}\right|1s(1)2p(2)1s(3)]\,, \tag{20}$$

where $a(1,2)$ is a solution of

$$(-\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - 1/r_1 - 1/r_2 + 1)a(1,2) + (1/r_{12} - \tfrac{5}{8})1s(1)1s(2) = 0\,. \tag{21}$$

Using an approximation for $a(1,2)$ in terms of a Legendre polynomial expansion, i.e.,

$$a(1,2) = \sum_{a,b,L} (r_1^a r_2^b + r_1^b r_2^a) \times e^{-k(r_1+r_2)}(r_1r_2)^L P_L(w_{12})C(a,b,L)\,, \tag{22}$$

where the variational-perturbation procedure was employed to obtain coefficients $C(a,b,L)$, direct substitution of the expansion into Eq. (19) readily evaluates the integral. The use of the Legendre polynomial expansion rather than a Hylleraas expansion for $a(1,2)$ does not limit the accuracy since only terms corresponding to $L=1$ survive upon integration over the angles. Chisholm and Dalgarno,[3] and Chisholm, Dalgarno, and Innes,[8] have evaluated some of the integrals in calculating the ϵ_2 for $1s^22s\,^2S$ and $1s^22p\,^2P$ states of the three-electron atom. The author coded the evaluation of all three-electron integrals similar to Eq. (19). It was felt that this would lessen the chance of errors and certainly reduce the required algebra. In addition it gave an independent check of the evaluations of Chisholm and Dalgarno for the $1s^22s\,^2S$ state of the three-electron atom. For this case agreement was excellent. For the $1s^22p\,^2P$ state agreement was excellent, except for one integral which disagreed by a factor of two. They called this particular integral the dispersion term. This lowers their computed ϵ_2 for the $1s^22p\,^2P$ state slightly. The difference, however, is quite small.

Table III lists the three-electron contributions that were calculated for the states considered here. The contributions from the three-electron integrals grow more rapidly than do the pair contributions. The evaluation of any required three-electron integral is straightforward, but the procedure is complicated by the huge number of required integrals.

V. DEGENERACY

Table V lists the perturbation coefficients for

TABLE V. Comparison of the truncated sum through second order with Hartree-Fock energies [taken from E. Clementi, J. Chem. Physics 38, 996 (1963)].

Atom	State	E(HF) (a.u.)	E (present calculation)
Li	^2S	$-7.432\,726$	$-7.464\,649$
Be	^1S	$-14.573\,02$	$-14.644\,848$
B	^2P	$-24.529\,05$	$-24.594\,017$
C	^1S	$-37.549\,54$	$-37.624\,338$
C	^3P	$-37.631\,32$	$-37.680\,373$
N	^4S	$-54.400\,91$	$-54.414\,283$
N	^2P	$-54.228\,09$	$-54.301\,654$
N	^2D	$-54.296\,15$	$-54.320\,059$
O	^1S	$-74.610\,95$	$-74.650\,401$
O	^3P	$-74.809\,36$	$-74.836\,645$
O	^1D	$-74.729\,21$	$-74.736\,418$
F	^2P	$-99.409\,29$	$-99.421\,092$
Ne	^1S	$-128.547\,0$	$-128.565\,581$

TABLE VI. Comparison of ϵ_2 values with Scherr, Silverman, and Matsen (SSM).

State		SSM	Present calculation
$1s^2 2s$	^2S	-0.4089	-0.4081
$1s^2 2s^2$	^1S	-0.880	-0.8819
$1s^2 2s^2 2p$	$^2P^\circ$	-1.843	-1.8566
$1s^2 2s^2 2p^2$	^3P	-3.253	-3.2880
$1s^2 2s^2 2p^3$	$^4P^\circ$	-5.20	-5.1759
$1s^2 2s^2 2p^4$	^3P	-8.05	-8.1318
$1s^2 2s^2 2p^5$	$^2P^\circ$	-11.64	-11.7551
$1s^2 2s^2 2p^6$	^1S	-16.07	-16.2738

the calculated states. There are a number of degenerate states. The ϵ_1 entry for these states are the roots obtained by requiring the H_1 matrix to be diagonal. The ϵ_2 entries for these states should be modified slightly, also, because the degeneracy contributes to second order as well as to first order. Some effort was expended to evaluate these contributions. Their magnitude is small. It is felt that inclusion of contributions to ϵ_2 for many-electron systems, because of degeneracy, unnecessarily complicates the problem.

VI. COMPARISONS AND CONCLUSIONS

Table VI compares the results obtained here with Scherr, Silverman, and Matsen.[9] These authors used a semiempirical technique for recovering the perturbation coefficients from experimental data. The agreement is reasonably good. Table V compares the truncated sum through second order with Hartree-Fock energies for the neutral atoms.

TABLE VII. Predicted perturbation coefficients of the correlation energy.

State	$-\epsilon_1{}^c$	$-\epsilon_2{}^c$
$1s^2\,{}^1S$	0	$0.046\,663$
$2s\,{}^2S$	0	$0.053\,616$
$2p\,{}^2P$	0	$0.059\,117$
$2s^2\,{}^1S$	$0.011\,727$	$0.076\,476$
$2s2p\,{}^1P$	0	$0.113\,117$
$2s2p\,{}^3P$	0	$0.083\,788$
$2s^2 2p\,{}^2P$	$0.006\,922$	$0.149\,316$
$2s2p^2\,{}^2S$	0	$0.180\,481$
$2s2p^2\,{}^2P$	0	$0.196\,070$
$2s2p^2\,{}^4P$	0	$0.119\,435$
$2s2p^2\,{}^2D$	0	$0.168\,987$
$2p^2\,{}^1S$	$-0.011\,727$	$0.120\,399$
$2p^2\,{}^3P$	0	$0.081\,267$
$2p^2\,{}^1D$	0	$0.115\,268$
$2p^3\,{}^4S$	0	$0.113\,111$
$2p^3\,{}^2P$	$-0.006\,922$	$0.173\,914$
$2p^3\,{}^2D$	0	$0.169\,078$
$2s^2 2p^2\,{}^1S$	$0.011\,993$	$0.224\,782$
$2s^2 2p^2\,{}^3P$	$0.003\,095$	$0.226\,808$
$2s^2 2p^2\,{}^1D$	$0.003\,095$	$0.238\,239$
$2s2p^3\,{}^3S$	0	$0.229\,260$
$2s2p^3\,{}^5S$	0	$0.160\,559$
$2s2p^3\,{}^1P$	0	$0.328\,992$
$2s2p^3\,{}^3P$	0	$0.243\,416$
$2s2p^3\,{}^1D$	0	$0.286\,976$
$2s2p^3\,{}^3D$	0	$0.229\,496$
$2p^4\,{}^1S$	$-0.011\,993$	$0.273\,265$
$2p^4\,{}^3P$	$-0.003\,095$	$0.243\,176$
$2p^4\,{}^1D$	$-0.003\,095$	$0.287\,446$
$2s^2 2p^3\,{}^4S$	0	$0.308\,949$
$2s^2 2p^3\,{}^2P$	$0.015\,609$	$0.352\,493$
$2s^2 2p^3\,{}^2P$	0	$0.332\,222$
$2s2p^4\,{}^2S$	0	$0.363\,508$
$2s2p^4\,{}^2P$	0	$0.413\,819$
$2s2p^4\,{}^4P$	0	$0.315\,109$
$2s2p^4\,{}^2D$	0	$0.385\,580$
$2p^5\,{}^2P$	$-0.015\,609$	$0.404\,288$
$2s^2 2p^4\,{}^1S$	$0.007\,397$	$0.435\,917$
$2s^2 2p^4\,{}^3P$	0	$0.459\,549$
$2s^2 2p^4\,{}^1D$	0	$0.448\,606$
$2s2p^5\,{}^1P$	0	$0.563\,677$
$2s2p^5\,{}^3P$	0	$0.482\,014$
$2p^6\,{}^1S$	$-0.007\,397$	$0.584\,714$
$2s^2 2p^5\,{}^2P$	0	$0.603\,508$
$2s2p^6\,{}^2S$	0	$0.682\,151$
$2s^2 2p^6\,{}^1S$	0	$0.794\,377$

Table VII lists the predicted energy coefficients of the correlation energy for the states considered here. The correlation energy E_c is defined as

$$E_c = E_{\mathrm{nr}} - E_{\mathrm{HF}} , \tag{23}$$

where E_{nr} is the nonrelativistic energy and E_{HF}

is the Hartree-Fock energy for a state. To second order, E_{nr} is

$$E_{nr}=\epsilon_0 Z^2+\epsilon_1 Z+\epsilon_2 \ , \qquad (24)$$

and $$E_{HF}=\epsilon_0 Z^2+\epsilon_1^{HF} Z+\epsilon_2^{HF} \ . \qquad (25)$$

Then $$E_c=(\epsilon_1-\epsilon_1^{HF})Z+(\epsilon_2-\epsilon_2^{HF}) \ , \qquad (26)$$

and $$E_c=\epsilon_1^c Z+\epsilon_2^c \ . \qquad (27)$$

The predicted Z dependence of the correlation energy occurs for states which are degenerate.[10] The values for ϵ_2^{HF} were taken from Froese.[11]

The author feels that the procedure can be extended to more electron systems and to excited states of atoms with fewer electrons. The major difficulty seems to be the evaluation of the three-electron integrals. The calculations of the pair functions are quite simple. A typical running time of three minutes is sufficient for a 160-term pair function on the IBM 360 in double precision. It should be pointed out that most systems with more than 11 electrons are degenerate. Thus the perturbation expansion should give results which are quite competitive with the Hartree-Fock procedure, since the correlation energy will contain a term linear in Z. Indeed, Table V indicates that for the degenerate states, namely the 1*s* state of beryllium, the ^2P state of boron, the ^1S, ^3P, and ^1D states of carbon, and the ^1S state of oxygen, the truncated sum is considerably deeper than it is for the other entries, in comparison with the Hartree-Fock energies. All these states are degenerate. Most states of more complex atoms are also degenerate.

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