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Variational Calculation of the Multiplet Spacings in the Carbon Isoelectronic Sequence

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The electron configuration $(1s)^2(2s)^2(2p)^2$ has been treated as a two-electron problem with the outer two electrons moving in the central field produced by the spherically symmetric $(1s)^2(2s)^2$ charge clouds. The zeroth-order wave function is taken to be a Clebsch-Gordan combination of products of one-electron Hartree-Fock orbitals. This wave function is then multiplied by a variational function of the form $1+cr_{12}$ and $1+cr_{12}+c'(r_1-r_2)^2$ where c and c' are determined by the variational principle for each of the three multiplet levels. The amount by which the energy is lowered is added to the Hartree-Fock energies to obtain total energies, but it is the ratio of the multiplet spacings which is the main concern. The experimental value for this ratio is about constant and equal to approximately 1.13 for the sequence C through Ar. The Hartree-Fock ratio ranges from 1.43 for C to 1.49 for Ar. The technique used here gives a ratio which ranges from 1.10 for C to 1.37 for Ar which is in good agreement with experiment even though $2s$-$2p$ correlations have been neglected.

I. INTRODUCTION

It is well known that the Hartree-Fock theory gives good average energies and ionization energies for many-electron atoms but gives poor results for the multiplet spacings for open-shell atoms. This is because the multiplet spacings depend on the Slater-Condon parameters which are overestimated by about 20% when Hartree-Fock functions are used to calculate them. This is apparently due to the failure of the Hartree-Fock theory to adequately account for the electron correlations. In two previous papers,[1,2] we have applied an old technique due to Hylleraas[3] to the separate multiplet levels of the $(3d)^2$ and $(2p)^2$ electron configurations in an effort to correct the multiplet spacings. In each case, the zeroth-order wave functions were Clebsch-Gordan combinations of Hartree-Fock orbitals. In both configurations, a simple one-parameter correlation function was used and it was found that the multiplet spacings were overcorrected if average-of-configuration Hartree-Fock (HF) functions were used. However, in the case of $(2p)^2$, the ratio of the multiplet spacings for C, N^+, O^{++} was in good agreement with experimental values if unrestricted HF functions were used for each level. It is the purpose of this paper to extend the latter calculation to all carbonlike ions through Ar and to include an additional parameter in the correlation function. The results will be found to be in excellent agreement with experiment.

Sinanoğlu[4] has developed a many-electron theory that includes electron correlations in a nonempirical way and in which the Hartree-Fock one-electron orbitals can be used as a starting point. In the application of this theory, variational corrections to the HF orbitals are additive functions while in our work they are multiplicative. More recently Öksüz and Sinanoğlu[5] have studied various types of correlation effects in nonclosed shell atoms and have found that certain types of correlations are transferable from one atom to another for Z between 5 and 11. The Sinanoğlu papers demonstrate the dominance of pair correlations and provide a physical basis for correlation effects in atoms. A short review paper by Condon[6] compares several approaches to correlation effects along with pertinent references.

In Sec. II, an outline of the semiempirical technique developed in our two previous papers[1,2] is given, followed by results for the carbonlike ions through $\mathrm{Ar}(Z=18)$. Section IV contains some concluding remarks.

II. FORMULATION

An outline of the semiempirical method is given here, but more details are contained in Ref. 1. The approximation is introduced at the outset whereby the atom is replaced by a two-electron system with each electron moving in an effective potential $V(r)$ which includes the effect of the $(1s)^2$ $(2s)^2$ core electrons. If the unrestricted HF functions are used as the zeroth-order functions, then $V(r)$ also includes some screening of one of the outer $2p$ electrons on the other. In spite of the expected large $2s$-$2p$ correlations[7] resulting form the interpenetration of these orbitals, this "core" model seems justified if one is interested only in the multiplet spacings or in the ratio of these spacings. Indeed, the results seem to bear this out, especially for the lighter atoms.

The Hamiltonian can be written, in hartree a. u.,

$$H = -\tfrac{1}{2}\nabla_1^2 + V(r_1) - \tfrac{1}{2}\nabla_2^2 + V(r_2) + 1/r_{12} \;, \tag{1}$$

where the contribution from the core has been dropped since it will not enter the variational calculation. The zeroth-order approximation consists of taking the wave function as a combination of products of one-electron functions ϕ_{nlm} which are eigenfunctions of the operators H_1 and H_2, i.e.,

$$H_i\phi_{nlm}(\vec{r}_i) = [-\tfrac{1}{2}\nabla_i^2 + U(r_i)]\,\phi_{nlm}(\vec{r}_i) = E_{nlm}\phi_{nlm}(\vec{r}_i)\,, \quad \phi_{nlm}(\vec{r}_i) = R_{nl}(r_i)Y_{lm}(\theta_i\phi_i) \;. \tag{2}$$

Here $U(r_i)$ differs from $V(r_i)$ in that the former includes the screening effect of one electron on the other, i.e.,

$$V(r_i) = U(r_i) - Y(r_i) \;, \tag{3}$$

where $Y(r_i)$ is the screening function of one of the electrons on the other. Using Eqs. (2) and (3), the Hamiltonian can be written

$$H = H_1 + H_2 + 1/r_{12} - 2Y(r_1) \tag{4}$$

for equivalent electrons. In what follows, H_1 and H_2 will be taken as the unrestricted HF Hamiltonian thus making $\phi_{nlm}(\vec{r}_i)$ unrestricted HF (UHF) orbitals.

The two-electron wave functions which diagonalize H are obtained by forming linear combinations of products of the UHF functions according to the Clebsch-Gordan coefficients,

$$\Psi_{LM}^{0} = \sum_{m_1} C^{llL}_{m_1,M-m_1}\,\phi^{(1)}_{nlm_1}\phi^{(2)}_{nlM-m_1} \;. \tag{5}$$

The electron correlation is now included in a semiempirical manner by inserting the correlation factor in Eq. (5) to obtain

$$\Psi_{LM} = N^{-1/2}\Psi_{LM}^{0}[1 + cr_{12} + c'(r_1 - r_2)^2] \,, \tag{6}$$

where N is the normalization constant given by

$$N = (\Psi_{LM}^{0}[1 + cr_{12} + c'(r_1 - r_2)^2] \,|\, \Psi_{LM}^{0}[1 + cr_{12} + c'(r_1 - r_2)^2])$$

$$= 1 + 2c\langle r_{12}\rangle + c^2\langle r_{12}^2\rangle + 2c'\langle (r_1 - r_2)^2\rangle + c'^2\langle (r_1 - r_2)^4\rangle + 2cc'\langle r_{12}(r_1 - r_2)^2\rangle \;. \tag{7}$$

In Eq. (7), the angular brackets represent matrix elements of the indicated operator calculated using the uncorrelated functions of Eq. (5) as a basis. In Eqs. (6) and (7), the values of c and c' are to be determined by the variation method and are, of course, dependent on L.

It is easy to show, especially by matrix methods, that the modified wave functions of Eq. (6) are still eigenfunctions of L^2, L_z, S^2, and S_z. It is obviously an eigenfunction of S^2 and S_z since no spin-interaction terms were included in the Hamiltonian and since the correlation factor does not alter the spin part of the wave function. Thus, the spin part will be omitted in the calculation. Although the proof by matrix methods that the functions of Eq. (6) are still eigenfunctions of L^2 and L_z is simple, it is only necessary to observe that the correlation factor contains only relative electron coordinates, and therefore, cannot change the total orbital angular momentum or its z component. It is also worth noting that the correlated wave functions retain the symmetry properties of the uncorrelated functions since the correlation factor is symmetric in the exchange of the electron coordinates. This allows for the separate minimization of each multiplet energy.

The energy is

$$W = (\Psi_{LM}^{0}[1+cr_{12}+c'(r_1-r_2)^2]\,|H|\,\Psi_{LM}^{0}[1+cr_{12}+c'(r_1-r_2)^2])/N$$

$$= (\Psi_{LM}^{0}|[1+cr_{12}+c'(r_1-r_2)^2]H[1+cr_{12}+c'(r_1-r_2)^2]|\Psi_{LM}^{0})/N\,.$$

The numerator can be considered as the diagonal element of the operator

$$\bar{H} = H + c(r_{12}H + Hr_{12}) + c^2 r_{12}Hr_{12} + c'[(r_1-r_2)^2H + H(r_1-r_2)^2]$$

$$+ c'^2(r_1-r_2)^2H(r_1-r_2)^2 + cc'[r_{12}H(r_1-r_2)^2 + (r_1-r_2)^2Hr_{12}] \tag{8}$$

with the original uncorrelated wave functions of Eq. (5) as the basis. Details for evaluating these matrix elements can be found elsewhere[1,8] and will not be discussed here.

In Eq. (8), H is the Hamiltonian given by Eq. (4) with the screening function $Y(r_1)$ given by

$$Y(r_1) = (1/r_1)\textstyle\sum_k a_L^{(k)} Y_k(2p, 2p; r_1)\,, \tag{9}$$

where $$Y_k(2p, 2p; r_1) = \frac{1}{r_1^{k}}\int_0^{r_1} |R_{2p}(r_2)|^2 r_2^{k+2}\,dr_2 + r_1^{k+1}\int_{r_1}^{\infty} |R_{2p}(r_2)|^2 r_2^{-k+1}\,dr_2, \tag{10}$$

and $$a_L^{(k)} = \sum_{m_1 m_1'} C^{llL}_{m_1 M-m_1}\, C^{llL}_{m_1' M-m_1'}\, c^k(lm_1, lm_1')\,c^k(lM-m_1', lM-m_1)\,. \tag{11}$$

In Eq. (11), $c^k(lm, lm')$ are the results of integrating over the products of three spherical harmonics and for $(2p)^2$, $k = 0, 2$. Thus, the screening function will be slightly different for each multiplet level. An additional difference occurs through the use of UHF radial functions since the radial integrals will be slightly different for each multiplet level. This, alone, accounts for some of the electron correlations. This is referred to by Sinanoğlu as "orbital polarization".[5] Normally, the orbital energies arising from H_1 and H_2 in Eq. (8) could be dropped since they would not enter the variation calculation nor the multiplet spacings. However, the use of UHF functions requires that these energies be retained in the multiplet spacings.

The radial functions used here were the short analytical expressions derived by Clementi.[9] They are linear combinations of Slater-type orbitals having the form, for the $2p$ orbital,

$$R_{2p}(r) = a_1R_{l1}(r) + a_2R_{l2}(r) + a_3R_{l3}(r) + a_4R_{l4}(r)\,, \tag{12}$$

with $$R_{lk}(r) = \{(2\sigma_{lk})^{n_{lk}+1/2}/[(2n_{lk})!]^{1/2}\}\, r^{n_{lk}-1}\, e^{-\sigma_{lk} r}\,. \tag{13}$$

The energy of each multiplet term associated with the $(n, n-1)^2$ ground electronic configuration is now obtained by minimizing

$$W = \langle \bar{H} \rangle / N \tag{14}$$

with respect to c and c', using the proper uncorrelated wave functions for a given L as a basis.

III. RESULTS

The above calculation has been performed, as mentioned earlier, for the $(1s)^2\,(2s)^2\,(2p)^2$ isoelectronic sequence from C to Ar for the two cases (i) c' zero and (ii) c' not zero. The results are presented in Tables I–IV. The calculations were made on an IBM 360/50 computer and we expect the last two significant digits in the total energy to be uncertain due to roundoff error. These digits have been retained, however in Tables I and III for the total energies but they have been dropped in the other entries in these tables as well as in Tables II and IV. Because of this uncertainty, it was not practical to correct the total energies for the small changes in the Rydberg constant as one progresses to higher Z values. The ratio of the multiplet spacings, given by

$$\text{Ratio} = [E(^1S) - E(^1D)]/[E(^1D) - E(^3P)]\,, \tag{15}$$

and which is the primary concern of this paper, is

TABLE I. Results for c' equal to zero. All energies are in Hartree a.u., not mass corrected as explained in text.

Atom	Hartree-Fock total energy ^1S	^1D	^3P	Total energy with correlation ^1S	^1D	^3P	Effect on HF energy ^1S	^1D	^3P	Ratio HF	Expt.	This work
C	−37.54949	−37.63130	−37.68858	−37.60891	−37.65334	−37.69282	−0.059	−0.022	−0.004	1.428	1.127	1.125
N	−53.69009	−53.80735	−53.88797	−53.76261	−53.83202	−53.89235	−0.072	−0.025	−0.004	1.454	1.141	1.150
O	−72.84624	−72.99720	−73.10016	−72.92635	−73.02334	−73.10461	−0.080	−0.026	−0.004	1.466	1.142	1.193
F	−95.01078	−95.19471	−95.31957	−95.09590	−95.22185	−95.32408	−0.085	−0.027	−0.004	1.473	1.140	1.232
Ne	−120.18047	−120.39699	−120.54352	−120.26916	−120.42481	−120.54806	−0.089	−0.028	−0.004	1.478	1.138	1.263
Na	−148.35361	−148.60246	−148.77052	−148.44505	−148.63079	−148.77508	−0.091	−0.028	−0.004	1.481	1.141	1.287
Mg	−179.52914	−179.81020	−179.99968	−179.62270	−179.83894	−180.00427	−0.094	−0.029	−0.004	1.483	1.120	1.308
Al	−213.70643	−214.01957	−214.23040	−213.80166	−214.04864	−214.23500	−0.095	−0.029	−0.005	1.485	1.134	1.325
Si	−250.88502	−251.23017	−251.46234	−250.98167	−251.25958	−251.46696	−0.097	−0.029	−0.005	1.487	1.130	1.340
P	−291.06463	−291.44175	−291.69519	−291.16245	−291.47132	−291.69981	−0.098	−0.030	−0.005	1.488	1.125	1.352
S	−334.24506	−334.65408	−334.92877	−334.34386	−334.68383	−334.93341	−0.099	−0.030	−0.005	1.489	···	1.362
Cl	−380.42612	−380.86702	−381.16292	−380.52579	−380.89692	−381.16756	−0.100	−0.030	−0.005	1.490	···	1.371
Ar	−429.60770	−430.08044	−430.39756	−429.70808	−430.11048	−430.40221	−0.100	−0.030	−0.005	1.491	···	1.379

TABLE II. Variational parameter c for c' zero.

Atom	$c(^1S)$	$c(^1D)$	$c(^3P)$
C	0.398	0.196	0.073
N	0.400	0.195	0.072
O	0.392	0.193	0.072
F	0.385	0.191	0.071
Ne	0.379	0.190	0.071
Na	0.374	0.188	0.071
Mg	0.370	0.187	0.071
Al	0.366	0.187	0.070
Si	0.364	0.186	0.070
P	0.361	0.186	0.070
S	0.359	0.185	0.070
Cl	0.358	0.185	0.070
Ar	0.356	0.184	0.070

plotted in Fig. 1.

Several interesting observations can be made from the results. First, the ratio of the multiplet spacings is in good agreement with the experimental ratio, especially for the lighter atoms. Even though the agreement becomes worse with increasing Z, it is still better than the HF ratio, and to our knowledge, it is the best value that has appeared in the literature. This divergence in the agreement with the experimental values is easily explained. The value of c from either Table II or Table IV is very nearly constant for all three levels in going from C to Ar, but a plot of the average value of r_{12} shows that it decreases roughly as $1/Z$ as one would expect. Therefore, the product cr_{12} represents a decreasing correction to the HF wave function. In fact, the ratio is expected to approach the HF ratio for large Z, and Fig. 1 shows such a tendency. In Table IV, $|c'|$ increases almost linearly with Z for ^1S and ^1D, but $\langle (r_1 - r_2)^2 \rangle$ decreases roughly as $1/Z^2$ so this correction also decreases about like $1/Z$.

The second feature of the results has to do with the effect of spatial correlation on the HF energy. This effect is very nearly constant for ^3P and increases in the order ^3P, ^1D, ^1S. This is precisely what is necessary to correct the ratio. Furthermore, the effect on the ^1D and ^1S energies increases with increasing Z which is also in the right direction since the HF ratio begins to deviate more from the experimental value. Third, the effect on the HF energy represents the amount of the actual correlation energy which has been accounted for by this technique. Clementi[10] has estimated this correlation energy and comparison of our results with his shows that for the ^3P level only a very small fraction of this energy has been accounted for here. However, for ^1D the fraction is greater and for ^1S it is approximately 30%.

TABLE III. Results for c' not zero. All energies are in uncorrected hartree a.u.

Atom	Total energy with correlation ^1S	^1D	^3P	Effect on HF energy ^1S	^1D	^3P	Ratio This work
C	−37.60912	−37.65340	−37.69351	−0.060	−0.022	−0.005	1.104
N	−53.76365	−53.83203	−53.89274	−0.074	−0.025	−0.005	1.126
O	−72.92808	−73.02342	−73.10489	−0.082	−0.026	−0.005	1.170
F	−95.09814	−95.22200	−95.32430	−0.087	−0.027	−0.005	1.211
Ne	−120.27178	−120.42501	−120.54825	−0.091	−0.028	−0.005	1.243
Na	−148.44796	−148.63105	−148.77525	−0.094	−0.028	−0.005	1.270
Mg	−179.62586	−179.83923	−180.00442	−0.097	−0.029	−0.005	1.292
Al	−213.80501	−214.04897	−214.23513	−0.098	−0.029	−0.005	1.310
Si	−250.98519	−251.25994	−251.46708	−0.100	−0.030	−0.005	1.326
P	−291.16609	−291.47170	−291.69993	−0.101	−0.030	−0.005	1.339
S	−334.34762	−334.68423	−334.93352	−0.102	−0.030	−0.005	1.350
Cl	−380.52966	−380.89734	−381.16767	−0.104	−0.030	−0.005	1.360
Ar	−429.71203	−430.11092	−430.40231	−0.104	−0.030	−0.005	1.369

TABLE IV. Variational parameters c and c'.

	^1S		^1D		^3P	
Atom	c	c'	c	c'	c	c'
C	0.411	−0.012	0.191	0.005	0.061	0.014
N	0.426	−0.034	0.197	−0.003	0.063	0.014
O	0.422	−0.052	0.198	−0.009	0.064	0.015
F	0.416	−0.067	0.197	−0.015	0.065	0.016
Ne	0.411	−0.081	0.197	−0.020	0.065	0.017
Na	0.406	−0.095	0.196	−0.025	0.065	0.018
Mg	0.402	−0.108	0.196	−0.030	0.065	0.019
Al	0.399	−0.122	0.196	−0.035	0.065	0.021
Si	0.396	−0.135	0.196	−0.040	0.065	0.022
P	0.394	−0.148	0.195	−0.044	0.065	0.023
S	0.392	−0.160	0.195	−0.049	0.066	0.024
Cl	0.390	−0.173	0.194	−0.054	0.066	0.025
Ar	0.388	−0.186	0.194	−0.058	0.066	0.027

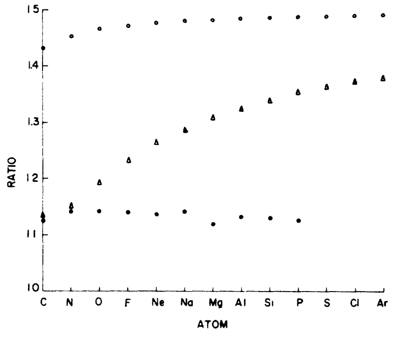

FIG. 1. Ratio of multiplet spacings versus atomic number for the $(1s)^2(2s)^2(2p)^2$ electron configuration. open circle, HF ratio; open triangle, this work; closed circle experimental ratio.

This apparently reflects the significance of the $2s$-$2p$ correlations which have been neglected here. If this is so, then these correlations must become less significant for the higher-lying singlet levels since we are able to account for more of the total correlation energy by a technique which neglects them. This suggests a more physical argument for the Z dependence of the ratio in Fig. 1. More of the $2s$-$2p$ correlations would cancel out in the numerator of Eq. (15) than in the denominator, thus as the central field becomes stronger the parallel-spin p electrons penetrate the $2s$ orbitals more than the antiparallel-spin electrons causing larger $2s$-$2p$ interaction for the triplet level. If this were included, it is possible that the ratio could be made less Z-dependent.

IV. CONCLUSION

The ratio of the multiplet spacings can be improved over the HF values by a rather simple semiempirical technique. The angular correlations dominate the pure radial correlations for all atoms, although the *relative* significance of these two effects is changed as Z increases. A more judicious choice of variational function could improve the ratio even more. In fact, it has been suggested[11] that a simultaneous variation of the HF orbital parameters and the correlation parameters should make further improvement. Indeed, this proved to be the case in the He sequence.[12]

About 30% of the total correlation energy can be accounted for by spatial correlation for the ^1S level and a lesser fraction for ^1D and ^3P. The $2s$-$2p$ correlations are more important for parallel-spin electrons than for antiparallel-spin electrons when the central field becomes strong enough to cause an abnormally large amount of interpenetration of the s and p orbitals.

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Correlation Energies of the $1s^2\,3l\;^2L$ States of the Lithium Sequence

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The nonrelativistic eigenvalues of the $(1s^2 3l\,^2L)$ states of the lithium sequence are calculated correct to second order in inverse powers of the nuclear charge. For large nuclear charges the addition of a $3l$ electron to the $1s^2\,^1S$ core increases the magnitude of the correlation energy by, respectively, 0.056, 0.092, and 0.034 eV for $l = 0$, 1, and 2. Most of the correlation arises from the pair energies.

I. INTRODUCTION

If the eigenvalue E of a many-electron atomic state is expressed as a series expansion in inverse powers of the nuclear charge Z according to

$$E = Z^2E_0 + ZE_1 + E_2 + Z^{-1}E_3 + \cdots , \qquad (1)$$

the evaluation of E_0 and E_1 is trivial and the coefficients E_2 and E_3 can be derived from electron-pair eigenfunctions.[1-4] Seung and Wilson[4] have so calculated E_2 and E_3 for the $1s^22s\,^2S$ states of the lithium isoelectronic sequence.

The coefficients E_2 and E_3 can also be expressed as summations of one- and two-particle matrix elements[5,6] and extensive calculations of E_2 have been carried out for the configurations $1s^22s^b\,2p^c$.[7] The second-order energy E_2 can be written as a weighted sum of electron-pair energies and certain single-electron energies.[1,3,6] The appropriate expressions have been developed for the $1s^22s\,^2S$ and $1s^22p\,^2P^\circ$ states of the lithium sequence and accurate values of E_2 have been cal-