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Semiempirical Electron Correlation in the Carbon Atom

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An empirical method of including the correlation of the two valence electrons has been applied to the carbon atom, which has a $(1s)^2(2s)^2(2p)^2$ ground electronic configuration. The carbon atom was chosen as a test of the method because of the penetrating nature of the $2p$ orbital. The atom was taken as a two-electron system with each electron moving in some kind of effective potential. The choice of this effective potential determines the type of raidal function to use as well as the screening function of one of the valence electrons on the other. For each choice of effective potential, a correlation factor $(1+cr_{12})$ is inserted into the wave function of each of the multiplet members obtained as Clebsch-Gordan combinations of one-electron orbitals, and the values of c are determined by the variation method. It is found that the ratio of multiplet spacings is very sensitive to the type of effective potential used and that the Hartree-Fock average of the configuration calculation gives the best results. In this calculation, the use of the correlated wave function gives a value for the ratio of the multiplet spacings of 1.34, compared with 1.43 obtained from the unrestricted Hartree-Fock calculation and 1.13 from experiment.

I. INTRODUCTION

IN the theory of multiplet structure of a two-electron configuration, such as $(2p)^2$, the wave functions of the various terms are usually taken as Clebsch-Gordan combinations of one-electron orbitals.[1,2] The multiplet spacings are found to depend on, in the case of $(2p)^2$, a single Slater-Condon integral and the ratio of the multiplet spacings is independent of this integral and has the value of 1.5 which is always considerably higher than the experimental value. There are two methods that can be used to correct this situation: (1) The Slater-Condon integral can be treated as an adjustable parameter chosen to fit the experimental values of the levels. This method may or may not give a better value of the ratio δ of the multiplet spacings. For example, if the same value of the Slater-Condon parameter is found which best fits all three multiplet levels in the p^2 configuration, δ would still be 1.5. Empirical values of the parameter have already been reported in the literature.[3,4] (2) The other method which can be used is the direct evaluation of the Slater-Condon integral from the exact wave function of the $2p$ electrons. Both of these methods include the effect of electron correlations; the first method does so in a purely empirical manner, while the second method would contain the correlation effect exactly and would, indeed, provide a physical basis for the first method. The difficulty with the second method, however, is the unavailability of exact many-electron wave functions.

Sinanoğlu[5] 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. This theory alleviates extensive configuration interaction calculations and provides the basis for a more accurate determination of the multiplet differences which are important in electronic spectra, core polarization, and molecular dissociation. While providing the proper quantitative basis for the empirical methods, the theory is rather complicated to use and, in many cases, a less sophisticated method which is intermediate between the exact theory and the empirical methods is adequate. For example, such an "intermediate" theory might be used to determine the order of the singlet and triplet states in large atoms where Russell-Saunders coupling breaks down.

An "intermediate," or semiempirical theory, has

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[1] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1951).

[2] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. I.

[3] J. Hinze and H. H. Jaffe, J. Chem. Phys. **38**, 1834 (1963).

[4] W. M. Cady, Phys. Rev. **43**, 322 (1933); M. A. Catalan and M. T. Antunnes, Z. Physik **102**, 432 (1936); M. A. Catalan, F. Rohrlich, and A. G. Shenstone, Proc. Roy. Soc. (London) **A221**, 421 (1954); L. E. Orgel, J. Chem. Phys. **23**, 1819 (1955); M. Ostrofsky, Phys. Rev. **46**, 604 (1934); Y. Tanabe and S. Sugano, J. Phys. Soc. Japan **9**, 766 (1954); and Ref. 2 above.

[5] O. Sinanoğlu, Advan. Chem. Phys. **6**, 315 (1964).

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been developed and applied to the $(3d)^2$ configuration of some transition metal ions and it was found that the method improved, though overcorrected, the multiplet spacings of both Ti III and Cr V.[6] This method consists of inserting a correlation factor of the form $(1+cr_{12})$ into the wave function for the two valence electrons which were obtained from linear combinations of one-electron orbitals, and then using the variation method to determine the parameter c. Inherent in this method is the assumption of a "core" model for the atom. Because of this assumption and the use of a simple, one-parameter variational function, one cannot expect the results to be as accurate as the nonempirical theory. However, this variational approach can be formulated in a rather simple manner and does not involve a great deal of numerical computation. In most of the cases in which the method has been used, the results show an improvement over those obtained without the correlation factor.

In this paper, the semi-empirical method is applied to the ground electronic configuration of the carbon atom which gives rise to a ^3P term, a ^1D term, and a ^1S term. The evolution of the improvement in the results is followed through the use of various core models, beginning with the most crude hydrogenic model and ending with an "inexact Hartree-Fock average of configuration" (HFAC) model. It is found that the ratio δ from the HFAC model is in satisfactory agreement with the experimental value. In Sec. II, a brief description is given of the general method including a discussion of the Hamiltonian and wave function. The various models used along with the results obtained from them are given in Secs. III–VII. Section VIII is a discussion of the results.

II. GENERAL FORMULATION

In order to facilitate a discussion of this work, a brief outline of the method is given here. More details are contained in Ref. 6. 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 inner core. The way this core effect is included depends on the particular model used. This will be discussed in more detail later. The Hamiltonian is now written, in Hartree atomic units, as

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

The zeroth-order approximation consists of taking the wave function as a product of the one-electron wave functions ϕ_{nlm} which are eigenfunctions of the operator H_1 and H_2, i.e.,

$$H_i\phi_{nlm}(\mathbf{r}_i)=[-\tfrac{1}{2}\nabla_i^2+U(r_i)]\phi_{nlm}(\mathbf{r}_i)=E_{nlm}{}^0\phi_{nlm}(\mathbf{r}_i)\,,$$
$$\phi_{nlm}(r_i\theta_i\varphi_i)=R_{nl}(r_i)Y_{lm}(\theta_i\varphi_i)\,. \quad (2)$$

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

$$V(r_i)=U(r_i)-Y(r_i)\,, \quad (3)$$

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

$$H=H_1+H_2+(1/r_{12})-Y(r_1)-Y(r_2)\,. \quad (4)$$

For equivalent electrons this simplifies to

$$H=H_1+H_2+(1/r_{12})-2Y(r_1)\,. \quad (5)$$

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

$$\begin{aligned}\psi_{LM}{}^0(1,2)&=\textstyle\sum_{m_1} C_{m_1,M-m_1}{}^{Lll}\phi_{nlm_1}(1)\phi_{nl,M-m_1}(2)\\&=R_{nl}(r_1)R_{nl}(r_2)\textstyle\sum_{m_1} C_{m_1,M-m_1}{}^{Lll}\\&\qquad\times Y_{lm_1}(\theta_1\varphi_1)Y_{l,M-m_1}(\theta_2\varphi_2)\,. \quad (6)\end{aligned}$$

The electron correlation is now included in a semi-empirical manner by inserting the correlation factor in Eq. (6) to obtain

$$\psi_{LM}=N^{-1/2}\psi_{LM}{}^0(1+cr_{12})\,, \quad (7)$$

where N is the normalization constant given by

$$\begin{aligned}N&=(\psi_{LM}{}^0(1+cr_{12})\,|\,\psi_{LM}{}^0(1+cr_{12}))\\&=1+2c\langle r_{12}\rangle+c^2\langle r_{12}{}^2\rangle\,. \quad (8)\end{aligned}$$

In Eq. (8), the angular brackets represent matrix elements of the indicated operator calculated using the uncorrelated functions of Eq. (6) as a basis. In Eqs. (7) and (8), the correlation coefficient c is to be determined by the variation method and is, of course, dependent on L.

It is easy to show, especially by matrix methods, that the modified wave functions of Eq. (7) 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. For L^2, L_z, recall that the angular dependence of r_{12} is the same as for $(1/r_{12})$ which is known to be diagonal in L, M but not in n, l. This is unlike the correlated wave functions in the Sinanoğlu theory. As shown by McKoy,[7] the wave functions there are not always eigenfunctions, separately, of the angular momentum, and therefore cannot always be minimized separately. The difference depends on the place in which the proper symmetry requirements are imposed on the wave function. Here, these symmetry requirements are built in at the outset in writing Eq. (6).

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[6] R. W. Mires and C. C. Lin, Phys. Rev. **134**, A332 (1964).

[7] V. McKoy, J. Chem. Phys. **43**, 1605 (1965).

TABLE I. Results for the hydrogenic-core model. All energies are in Hartree atomic units, e^2/a where a is the Bohr radius for the respective atom, i.e., a includes the proper reduced mass. One-electron orbital energies are included.

Atom	Level	c	Calculated energy No corr.	Calculated energy With corr.	Energy difference
C I	^1S	0.670076	−2.504785	−2.609548	0.104763
	^1D	0.261607	−2.607617	−2.640508	0.032891
	^3P	0.078197	−2.676171	−2.680801	0.004630
N II	^1S	0.581593	−4.337988	−4.451177	0.113189
	^1D	0.244413	−4.472461	−4.506738	0.034277
	^3P	0.076005	−4.562109	−4.566787	0.004678
O III	^1S	0.534578	−6.671191	−6.789910	0.118719
	^1D	0.234489	−6.837305	−6.872458	0.035153
	^3P	0.074695	−6.948047	−6.952753	0.004706

Atom	Spacing	Observed Energy[a]	δ	Calculated No corr.	δ	Calculated With corr.	δ	% Error
C I	$^1S-{}^1D$	0.052190		0.102837		0.030580		41.4
	$^1D-{}^3P$	0.046315	1.13	0.068549	1.5	0.040674	0.75	12.2
N II	$^1S-{}^1D$	0.079155		0.134473		0.055562		29.8
	$^1D-{}^3P$	0.069380	1.14	0.089648	1.5	0.060048	0.93	13.4
O III	$^1S-{}^1D$	0.104400		0.166114		0.082552		20.9
	$^1D-{}^3P$	0.091415	1.14	0.110741	1.5	0.080291	1.03	12.2

[a] Observed values taken from Slater, Ref. 2.

The energy is

$$W=(\psi_{LM}^0(1+cr_{12})|H|\psi_{LM}^0(1+cr_{12}))/N$$
$$=(\psi_{LM}^0|(1+cr_{12})H(1+cr_{12})|\psi_{LM}^0)/N. \qquad (9)$$

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

$$\bar{H}=H+c(r_{12}H+Hr_{12})+c^2r_{12}Hr_{12}, \qquad (10)$$

with the original uncorrelated wave functions of Eq. (6) as the basis. Details for evaluating these matrix elements are given in Ref. 6.[8] The energy of each multiplet term associated with the $(n, n-1)^2$ ground electronic configuration is obtained by minimizing

$$W=\langle\bar{H}\rangle/N \qquad (11)$$

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

The various models, to be discussed next, will differ from each other in the choice of $U(r_i)$ and $Y(r_i)$. This choice will also determine implicitly the type of radial functions to use.

III. HYDROGENIC-CORE MODEL

In this section, the semiempirical theory will be applied to two $2p$-electrons where each electron moves in a purely hydrogenic type of central field. This is referred to as the hydrogenic-core (HC) model and it implies that the one-electron radial functions should be of hydrogenic type and that the screening function $Y(r)$ should be of the form

$$Y(r)=\sigma/r, \qquad (12)$$

where σ is a constant since only then will the central field be hydrogenic in form. Also $U(r)$ is taken as

$$U(r)=Z'/r, \qquad (13)$$

where Z' is identified as the effective charge which makes the one-electron orbital an eigenfunction of the one-electron Hamiltonian given in Eq. (2). By Slater's rules for effective nuclear charge,[9] Z' should be 3.25 for C, 4.25 for N^+, 5.25 for O^{++}, etc. The same set of rules also gives σ to be 0.35. These values are used and the results are shown in Fig. 1 and in Table I. In Fig. 1, the decrease in the value of the correlation coefficient c with increasing Z' is to be expected since, as the central field becomes stronger, the intraelectron interactions plays a lesser role in determining the multiplet energies. The same reason is given for the improvement in the calculated ratio δ with increasing Z' as shown in Table I. The individual multiplet separations are also given in Table I, where the percentage error is calculated using the observed value as a standard. The $^1D-{}^3P$ separation is over-corrected, but otherwise it is in rather good agreement with the observed value. However, in each case, the $^1S-D^1$ separation is considerably over-corrected. This deviation must be attributed to the ^1S level alone, which lies so high in energy that, for a given Z', the hydrogenic orbitals become a poor basis set for the unperturbed Hamiltonian.

IV. UNRESTRICTED STO MODEL

In the unrestricted Slater-type orbital (USTO) model the radial function is a single Slater-type orbital (STO), identical with the hydrogenic function for a $(n, n-1)$ electron, and $U(r)$ is again given by Eq. (13). However,

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[8] Equation (14) in Ref. 6 should read $\langle r_{12}H_1\rangle=\langle H_1r_{12}\rangle=E_{nlm}^0\langle r_{12}\rangle$.

[9] See Ref. 2.

the screening constant σ in $Y(r)$ is now an explicit function of r, i.e., $Y(r)$ is taken to be

$$Y(r_1)=\frac{1}{r}\sum_k a_L^{(k)}Y_k(2p,\,2p;\,r_1)\,, \tag{14}$$

where

$$Y_k(2p,\,2p;\,r_1)=\frac{1}{r^k}\int_0^{r_1}|R_{2p}(r_2)|^2 r_2^{k+2}dr_2 + r_1^{k+1}\int_{r_1}^{\infty}|R_{2p}(r_2)|^2 r_2^{-k+1}dr_2\,, \tag{15}$$

and

$$a_L^{(k)}=\sum_{m_1m_1'} C_{m_1M-m_1}{}^{Lll}C_{m_1'M-m_1'}{}^{Lll} \times c^k(lm_1,lm_1')c^k(lM-m_1',\,lM-m_1)\,. \tag{16}$$

In Eq. (16), $C_{m_1M-m_1}{}^{Lll}$ are the well-known Clebsch-Gordan coefficients for two equivalent electrons and $c^k(lm,lm')$ are the result of integrating over the products of three spherical harmonics. Thus, $Y(r)$ is different for the different members of the multiplet, and since $U(r)$ implicitly contains this screening effect, Z' is not expected to be the same for all three multiplet levels. Therefore, Z' should be regarded as an orbital exponent rather than an effective charge. This means also that the one-electron orbital energies will not be the same for all the levels and, in calculating the ratio of the multiplet separations, these orbitals energies must be included. In Fig. 2 the correlation coefficient is plotted against the orbital exponent for this model. For almost all values of Z', the value of c is greater for the ^3P level than for either the ^1D or ^1S levels. This is contrary to what one expects. Intuitively, the value of c for the triplet state should be less than for the singlet states. This is because the symmetry of the uncorrelated wave function for ^3P should already include some correlation between electrons of the same spin, whereas it does not for the singlets. This should be reflected in a lower value for c for ^3P than for ^1D or ^1S. Thus, the USTO model will be abandoned without presenting any further results.

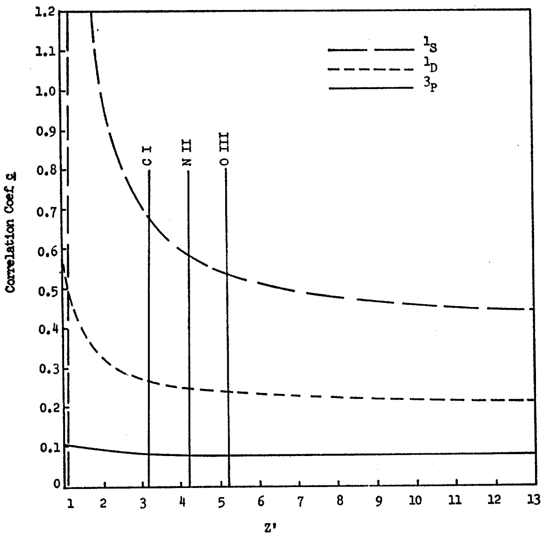

FIG. 1. Correlation coefficient versus Z' using the hydrogenic-core model with $Y(r)=0.35/r$.

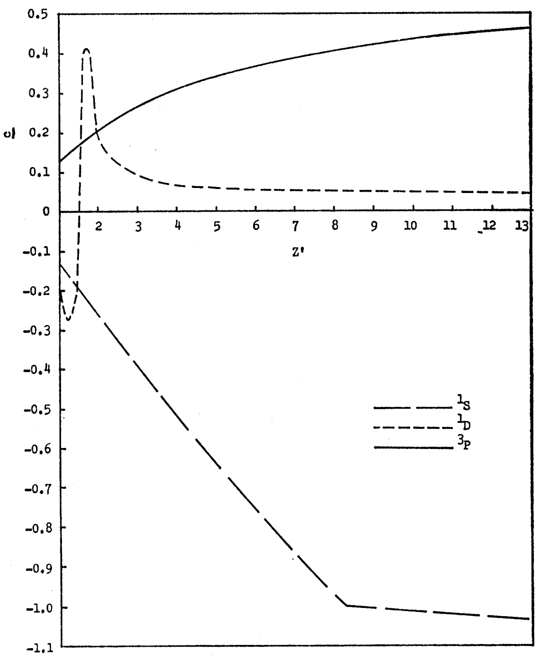

FIG. 2. Correlation coefficient versus Z' using the USTO model.

V. STO AVERAGE-OF-CONFIGURATION MODEL

The STO average-of-configuration (STOAC) model is identical with the USTO model except that the angular coefficients $a_L^{(k)}$ in Eq. (14) are averaged over the entire multiplet according to

$$a_c^{(k)}=\frac{\sum_{L,S}(2L+1)(2S+1)a_L^{(k)}}{\sum_{L,S}(2L+1)(2S+1)}\,. \tag{17}$$

This gives

$$a_c^{(0)}=1,\quad a_c^{(2)}=-2/25\,. \tag{18}$$

Thus, $Y(r_1)$ and Z' are the same for all three levels, but Z' can still be regarded as an orbital exponent. The one-electron orbital energies now subtract out in forming multiplet separations. The results are shown in Figs. 3 and 4 and are not qualitatively different from the USTO results.

VI. UNRESTRICTED HARTREE-FOCK MODEL

This UHF model uses the expression in Eq. (14) with the values of $a_L^{(k)}$ from Eq. (16) for the screening function. However, $U(r)$ is the self-consistent-field (SCF) expression which does not need to be written down since it will not enter the calculation explicitly.

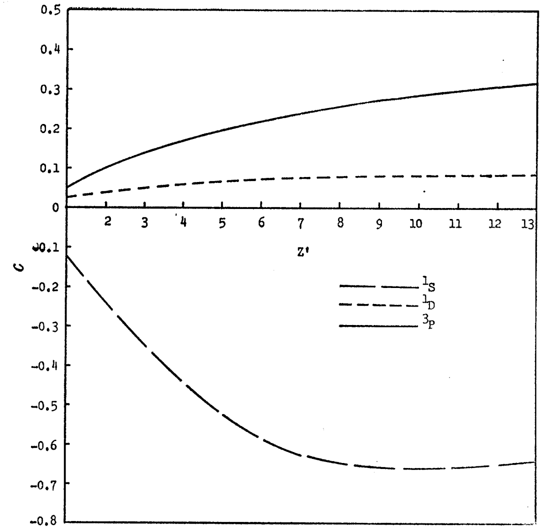

FIG. 3. Correlation coefficient versus Z' using the STOAC model.

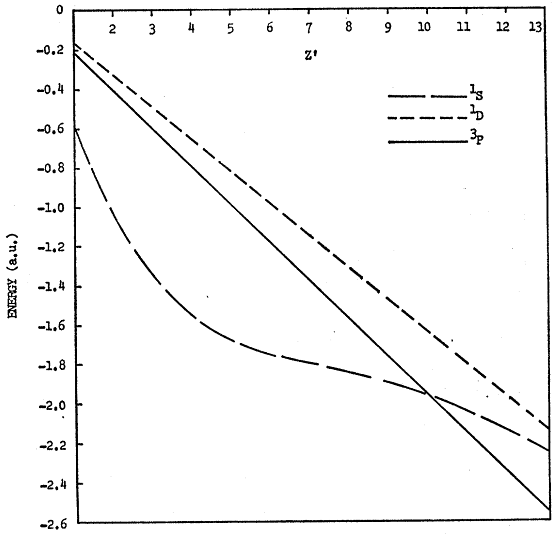

FIG. 4. Multiplet energy versus Z' using the STOAC model.

$U(r)$ determines the type of radial function to be used and the one-electron orbital energies. These two quantities will be slightly different for each of the three levels since $U(r)$ is slightly different because of L dependence of $a_L^{(k)}$. Clementi *et al.*[10] have used short analytical expressions for the radial functions and have obtained solutions to the SCF equations including the orbital energies. These radial functions are linear combinations of STO functions having the form, for the $2p$-orbital,

$$R_{2p}(r)=a_1R_{l1}(r)+a_2R_{l2}(r)+a_3R_{l3}(r)+a_4R_{l4}(r)\,, \tag{19}$$

where

$$R_{lk}(r)=\frac{(2\sigma_{lk})^{n_{lk}+1/2}}{[(2n_{lk})!]^{1/2}}r^{n_{lk}-1}e^{-\sigma_{lk}r}. \tag{20}$$

It is $R_{2p}(r)$ which is to be used in Eq. (15) as well as in all other radial integrals which arise in the calculation of Eq. (11). Again, the orbital energies must be included in the multiplet differences. Results for this model are shown in Table II. Again, the value of c is larger for the triplet than for the singlets. Also, the correlation has reordered the three levels.

TABLE II. Results for carbon using the UHF model. All energies are in Hartree units. One-electron orbital energies are included.

Level	c	Calculated energy No. Corr.	 With corr.	Energy difference
^1S	0.448398	−1.20683	−1.72004	0.51321
^1D	0.469016	−1.29499	−1.72224	0.42725
^3P	0.476786	−1.35660	−1.71439	0.35779

VII. INEXACT HF AVERAGE-OF-CONFIGURATION MODEL

Again, Eq. (17) is used in Eq. (14) so that $V(r_1)$ is the same for all three multiplet levels, provided that the same radial function is used. This radial function should be the solution of another SCF equation, which gives the best value for the average energy of the configuration. Such an "a-of-c" function is not available as yet, but is not expected to be significantly different from either one of Clementi's radial functions for carbon. Indeed, if Clementi's orbital energies are averaged over the configuration according to the procedure of Eq. (17), then the "a-of-c" energy is found to be

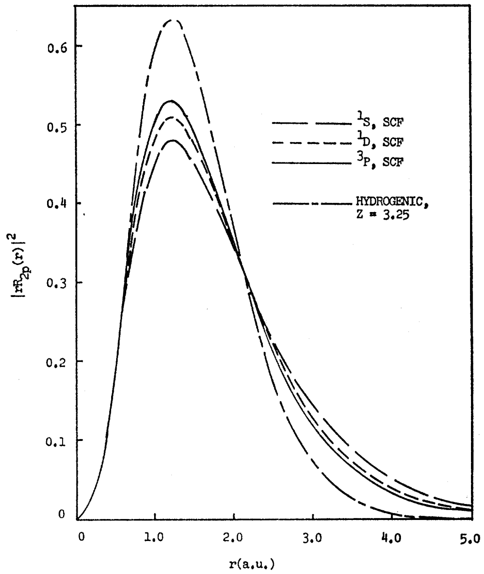

FIG. 5. Radial charge density for carbon.

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[10] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962).

TABLE III. Results for carbon using the HFAC model. All energies are in Hartree units. The average two-electron energy is omitted.

Level	c	Calculated energy		Energy difference	δ		
		No corr.	With corr.		UHF[a]	This work	Obs.
(a) ^1D radial functions are used							
^1S	0.570930	−0.391879	−0.848022	0.456143	1.4275	1.3407	1.1268
^1D	0.489386	−0.476139	−0.881881	0.405742			
^3P	0.442723	−0.532312	−0.907136	0.374824			
(b) ^3P radial functions are used							
^1S	0.593254	−0.402334	−0.868220	0.465886	1.4275	1.3386	1.1268
^1D	0.507055	−0.489918	−0.903428	0.413510			
^3P	0.457882	−0.548307	−0.929730	0.381423			

[a] Calculated from Clementi's total energies, Ref. 10.

about midway between the ^3P and ^1D energies. Also, from Fig. 5, the UHF ^1D radial charge density appears to be an acceptable compromise for all three levels. It is this function which was used to obtain the results shown in Table III. It can be seen that the ratio δ is in satisfactory agreement with the experimentally observed value. Table III also shows the same results using the ^3P radial function obtained by Clementi as if it were the correct "a-of-c" function. The value of δ is practically unchanged.

VIII. RESULTS

The results indicate that a satisfactory representation of the multiplet levels can be obtained from the semiempirical electron correlation theory if the HF average-of-configuration model is used. This is attributed to the sensitivity of the results to the proper radial function as well as the screening function. These two quantities are compared in Figs. 5 and 6. Apparently, the UHF model has already accounted for a large part of the electron interactions and the effect of the correlation factor is too strong, whereas the HFAC model does not include so much of the correlation and the correlation factor corrects this deficiency by a satisfactory amount. The HFAC model is also more accurate than the non-SCF models because the core is more accurately represented since the central field now contains interactions between the valence electrons and core electrons through the SCF potential.

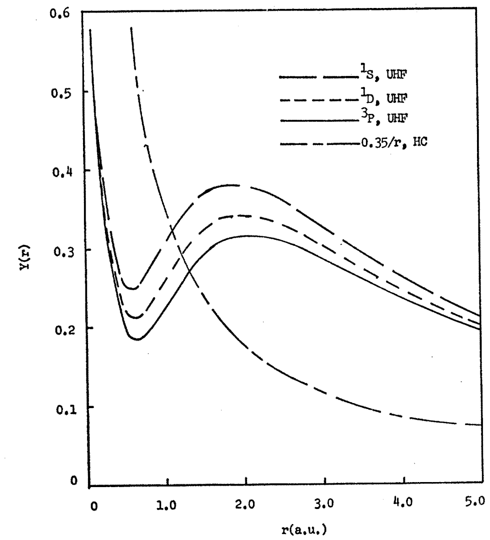

FIG. 6. Screening function for carbon. $Y(r)$ from HC model compared with $Y(r)$ for the three multiplet levels from the UHF model.

There is another consideration, however, which has to do with the core model. Since the $2s$ and $2p$ orbitals mutually interpenetrate quite strongly, one could undoubtedly expect more accurate results by treating the carbon atom as a four-electron problem with a core consisting of the $(1s)^2$ electrons. In fact, McKoy and Sinanoğlu[11] have found that the $2s$-$2p$ correlations are very large, about equal to the $2p$-$2p$ correlations. Since these produce corrections in the same direction as the p-p correlation, they would further improve the results of this calculation. However, such a semiempirical method as outlined here, based on a two-electron model, could be very useful for the $(ns)^2$, $(np)^2$, and $(nd)^2$ configurations of atoms and ions in which very little intershell correlations are expected.

While the results here show a definite improvement, the remaining deviation from the experimental results must be attributed to the naive choice of the core and to the use of a one-parameter correlation factor. Both of these effects are presently being studied.

ACKNOWLEDGMENTS

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[11] V. McKoy and O. Sinanoğlu, J. Chem. Phys. 41, 2689 (1964).