

are included in the basis set. The matrix elements $\langle \chi_{k'n} | W_1 | \chi_{k,l} \rangle$ have been computed in Ref. 5. $\langle \chi_{k'n} | \times W_1 P G_1^+ W_1 | \chi_{k,l} \rangle$ is evaluated numerically as described in Ref. 6. Equations (6) and (7) may then be solved and the three variation probabilities computed. In Table I we compare the results of a few such calculations with Secrest and Johnson exact values.⁷ We note a remarkable improvement in Eq. (9) over Eq. (4). The value given by Eq. (4) may be improved somewhat by using a trial ϕ , $|\phi^+_{kl}\rangle = |\chi_{kl}\rangle + \sum_j L_j |\chi_j\rangle$, where j

does not include $|\chi_{k,l}\rangle$. In all calculations where we included just a very few oscillator levels in the trial function (as in entry 3 of Table I), it was the inclusion of the projection operator in Eq. (3) which proved to be the essential step in obtaining a reasonably accurate value for the iterated P . In the calculations reported in Table I we have included enough momentum values for each oscillator state to ensure convergence to about 5% accuracy in the iterated P and the P calculated from Eq. (9).

Calculation of Energy Levels Which Arise from the p^2 Configuration of the Ground State of Carbon. Multiconfiguration Hartree-Fock Calculations

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A calculation of the term splitting (${}^3P-1D$)/($1D-1S$) for the p^2 ground-state configuration of carbon using Hartree-Fock radial orbitals gives an error of 21% when compared with experiment. Multiconfiguration Hartree-Fock calculations where the excitations are confined to the $2p^2$ shell reduces the error to slightly more than 1%.

I. INTRODUCTION

WHEN Hartree-Fock (HF) wave functions are used to calculate the relative energy levels of the different terms which arise from a given configuration, the results are generally in poor agreement with experiment; e.g., in the p^2 ground-state configuration in carbon the ${}^3P-1D$ transition is in error by somewhat less than 30%, the ${}^3P-1S$ transition by somewhat more than 40%.

Evidently a correlated function must be used to study this problem. Two approaches to the introduction of correlation into the wave function may be used. One could try to calculate very good approximate wave functions which include nearly all the correlation energy, or one could try to calculate wave functions for the three states mentioned above which would have very nearly the *same errors* in their energies. Although the absolute errors in the total energies may be relatively large, the errors in the *differences* in the total energies for all three states would be small. The second approach seems to us to be preferable since it is certainly much more likely to be extendable to large systems.

Even though methods are now available to obtain a very large fraction (>90%) of the correlation energies of the closed-shell configuration $1S$ states of first-row atoms, the extension to states which arise from open-shell configurations even of first-row atoms presents formidable difficulties in practice if not in principle. The term splitting in the ground-state configurations

of first-row atoms is not a very exciting physical problem. Interesting problems only arise much farther down the periodic table where it would be extremely difficult to try to use many if not most of the methods which have been used for calculating wave functions for the $1S$ ground states of He and Be.

The difficulty in applying an approximate method (like HF) to physical problems is not so much that errors are introduced but that the errors are different for different states. For many problems all one really needs to do is to modify the approximate method so as to obtain a roughly constant error. Thus, in the study of energy levels which arise from the same configuration we need only add enough correlation energy so that we find roughly the same error in each state.

The method which seems to us most promising to fulfill this goal at the present time is the multiconfiguration Hartree-Fock method (MCHF). In this method variational equations are solved for both the orbitals which are used to construct the configurations and the coefficients of the configurations in the wave functions. Iterations are repeated until self-consistent values are obtained for both orbitals and configuration-mixing coefficients. The procedure was probably first described by Frenkel¹ and the first calculations were carried out with two configurations for some states of 0 , 0^+ , and 0^{++} by Hartree, Hartree, and Swirles.² Since the 1940's MCHF calculations on atomic energy levels have been

¹ J. Frenkel, *Wave Mechanics, Advanced General Theory* (Clarendon Press, Oxford, England, 1934).

² D. R. Hartree, W. Hartree, and B. Swirles, *Phil. Trans. Roy. Soc. London A238*, 223 (1939).

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TABLE I. Properties of multiconfiguration wave function for 3P , 1D , and 1S states of carbon.

State	Configuration	Wave-function type			
		1 Configuration	2 Configurations	4-5 Configurations	3-4 Configurations
3P	$1s^2 2s^2 2p^2$	1.0 ^b	0.98884 ^b	0.98695 ^b	0.99770 ^b
	$1s^2 2p^4$		0.14898	0.14687	
	$1s^2 2s^2 3p^2$			0.04960	0.05150
	$1a^2 2s^2 3d^2$			0.04350	0.04418
	E (a.u.)	-37.688625	-37.705994	-37.714845	-37.697765
	ΔE_{calc}	0	0	0	0
	ΔE_{obs}^a	0	0	0	0
$F^2(2p, 2p)$ (cm ⁻¹)	53398.5	53850.7	53723.3	53259.5	
1D	$1s^2 2s^2 2p^2$	1.0	0.98913	0.98610	0.996283
	$1s^2 2p^4$		0.14706	0.14380	
	$1s^2 2s^2 3p^2$			0.06896	0.07188
	$1s^2 2s^2 3d^2$			0.04434	0.044508
	$1s^2 2s^2 3s 4d$			0.01465	0.01486
	E	-37.631348	-37.648119	-37.661163	-37.644821
	ΔE_{calc}	0.0573	0.0579	0.0537	0.0529
ΔE_{obs}^a	0.0464	0.0464	0.0464	0.0464	
$F^2(2p, 2p)$ (cm ⁻¹)	51371.6	51953.5	51712.7	51110.5	
1S	$1s^2 2s^2 2p^2$	1.0	0.96355	0.95859	0.99013
	$1s^2 2p^4$		0.26953	0.25549	
	$1s^2 2a^2 3p^2$			0.08799	0.10263
	$1s^2 2s^2 3d^2$			0.08479	0.08968
	$1s^2 2s^2 3s^2$			0.02994	0.03224
	E	-37.549618	-37.610368	-37.642993	-37.585816
	ΔE_{calc}	0.1390	0.0956	0.0719	0.1119
	ΔE_{obs}^a	0.0986	0.0986	0.0986	0.0986
	$F^2(2p, 2p)$ (cm ⁻¹)	48254.3	50693.9	50600.1	48141.8
	$[\langle {}^3P-{}^1D/{}^1D-{}^1S \rangle]_{\text{calc}}$	0.7013	1.5358	2.9505	0.8966
$[\langle {}^3P-{}^1D/{}^1D-{}^1S \rangle]_{\text{obs}}$	0.8899	0.8899	0.8899	0.8899	

^a C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. (U.S.) Circ. No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).

^b Mixing coefficients.

carried out by Jucys and co-workers³ although their method is not identical with that of Hartree, Hartree, and Swirls.

One can use MCHF functions to obtain a very large percentage of the correlation energy; e.g., Vizbaraitė *et al.*⁴ have found that a seven-configuration ($1s^2, 2s^2, 2p^2, 3d^2, 3p^2, 2p3p$) MCHF function for the 1S ground state of He gives an energy of -2.9000 atomic units (a.u.) which represents 91% of the correlation energy. We feel the power of the method is not so much in calculating nearly all the correlation energy of small systems but in making it possible to selectively add those configurations which will reduce the problem of spectra to the "same error" approximation whether this be for small or large systems.

In this paper we have chosen to study the simplest possible case of term splitting in the same configuration, namely, the p^2 ground-state configuration of carbon, and we report results for three different MCHF functions for each of the states 3P , 1D , and 1S . As far as we know the only previous calculation of MCHF functions for these states of carbon is the two-configuration

calculation of Clementi and Veillard⁵ for the 3P state. Jucys⁶ has calculated a multiconfiguration function of carbon but with neglect of exchange.

II. RESULTS

In the MCHF calculations given in this paper, all configurations have been built from a single set of orthonormal functions. The orbitals have the usual central field form:

$$\varphi_{nlm_l m_s}(\mathbf{x}) = R_{nl}(r) Y_{lm_l}(\theta, \varphi) n m_s, \quad (1)$$

and the same radial function R_{nl} is used for all m_l and m_s values. The configurations all differ from each other by at least double replacements. The derivation of the variational equation and the method of solution are straightforward and well known.² These equations have been solved without further approximation. The calculations have been performed using the numerical analysis and the computer program developed by Froese.⁷ The program has been modified in the course of this work to facilitate convergence of the calculations.

Four sets of calculations have been performed for each of the terms 3P , 1D , and 1S . These are: (1) the usual one-configuration HF calculations; (2) two-

³ For a recent paper, see A. P. Jucys *et al.*, *Opt. i Spectroskopiya* **12**, 157 (1962) [English transl. *Opt. Spectry.* **12**, 83 (1962)].

⁴ I. Vizbaraitė, V. Shironas, V. Kavetskis, and A. P. Jucys, *Opt. i Spectroskopiya* **1**, 277 (1956) [English transl.: Air Force Cambridge Research Laboratories Report No. T-R-471 (unpublished)].

⁵ E. Clementi and A. Veillard, *J. Chem. Phys.* **44**, 3050 (1966).

⁶ A. P. Jucys, *Zh. Eksperim. i Teor. Fiz.* **19**, 565 (1949) [English transl.: NASA Report No. NASA-TT-F154, 1963 (unpublished)].

⁷ C. Froese, *Can. J. Phys.* **41**, 1895 (1963); and (unpublished).

TABLE II. Properties of orbitals in multiconfiguration wave functions for 3P , 1D , and 1S states of carbon (in a.u.).

State	Orbital	1 Configuration			Wave function 2 Configurations			Type 4-5 Configurations			3-4 Configurations		
		ϵ	$ A_0 $	$\langle r \rangle$	ϵ	$ A_0 $	$\langle r \rangle$	ϵ	$ A_0 $	$\langle r \rangle$	ϵ	$ A_0 $	$\langle r \rangle$
3P	1s	-11.3255	27.6779	0.2684	-11.3161	27.7467	0.2669	-11.3167	27.7474	0.2669	-11.3262	27.6777	0.2684
	2s	-0.7056	5.8972	1.5893	-0.7211	5.5201	1.5874	-0.7215	5.5660	1.5872	-0.7063	5.8984	1.5890
	2p	-0.4333	6.0859	1.7145	-0.4449	6.1077	1.7028	-0.4537	6.1062	1.7058	-0.4426	6.0981	1.7179
	3p							-1.2928	10.4115	2.2508	-1.2754	10.3343	2.2703
	3d							-1.6756	4.1854	1.8195	-1.6961	4.1815	1.8237
1D	1s	-11.3515	27.6800	0.2684	-11.3414	27.7480	0.2669	-11.3426	27.7493	0.2668	-11.3528	27.6796	0.2684
	2s	-0.7187	5.9271	1.5882	-0.7327	5.5998	1.5816	-0.7336	5.5913	1.5819	-0.7200	5.9268	1.5823
	2p	-0.3813	5.9853	1.7720	-0.3939	6.1077	1.1555	-0.4072	6.0239	1.7616	-0.3956	6.0059	1.7789
	3s							-2.456	7.4207	2.0294	-2.4094	7.3635	2.0465
	3p							-1.1963	9.5504	2.3040	-1.1750	9.4809	2.3307
	3d							-1.5809	3.4564	1.8549	-1.560	3.4169	1.8669
	4d							-1.2673	8.0193	2.0304	-1.2391	7.9326	2.0470
1S	1s	-11.3916	27.6829	0.2683	-11.3564	27.7534	0.2668	-11.3568	27.7567	0.2667	-11.3920	27.6826	0.2683
	2s	-0.7397	5.9133	1.5713	-0.7852	5.6254	1.5680	-0.7824	5.6044	1.5695	-0.7402	5.9713	1.5719
	2p	-0.3101	5.8333	1.8706	-0.3556	6.1077	1.7938	-0.3849	5.9485	1.7957	-0.3466	5.8599	1.8732
	3s							-1.1644	6.9194	2.2419	-1.0624	6.6680	2.3345
	3p							-1.1494	9.0532	2.3202	-1.0501	8.6941	2.4460
3d							-1.5550	3.2870	1.8523	-1.4547	3.0873	1.9154	

configuration calculations with the ground configuration $1s^2 2s^2 2p^2$ and the quasidegenerate configuration⁸ $1s^2 2p^4$; (3) four- or five-configuration calculations including the two configurations of set (2), all allowed configurations of the form $1s^2 2s^2 3l^2$, and for the 1D state the configuration $1s^2 2s^2 3s 4d$; and (4) three- or four-configuration calculations which include the configurations of set (3) but without the quasidegenerate configuration $1s^2 2p^4$. For all the configurations used, only one term with the desired L and S values could be constructed; thus the choice of state was unique. We attempted to use in place of the configuration $1s^2 2s^2 3s 4d$, the configuration $1s^2 2s^2 3s 3d$. We were not, however, able to obtain a converged solution using a single d orbital when both the configurations $1s^2 2s^2 3d^2$ and $1s^2 2s^2 3s 3d$ were included. The $3d$ and $4d$ orbitals occupy essentially the same region of space as may be seen from the fact that $\langle r \rangle_{3d} = 1.9$ and $\langle r \rangle_{4d} = 2.0$ a.u.

In Table I, we give for each calculation the configuration mixing coefficients; the total energy in a.u.; the calculated energy relative to the 3P term energy obtained for the same set, labelled ΔE_{calc} ; the observed energy relative to the 3P term, labelled ΔE_{obs} ; and the value of the Slater integral $F^2(2p, 2p)$ in cm^{-1} . In addition, we compare, for each set of calculations, the calculated and observed values of the term interval ratio, $({}^3P - {}^1D)/({}^1D - {}^1S)$.

In Table II, we give the values of the orbital properties ϵ_{nl} , $\langle r \rangle_{nl}$, and $A_0(nl)$, all in atomic units. The values of ϵ_{nl} are usually referred to as orbital energies but, especially for the orbitals not in the ground configuration, it is better to regard them as simply the diagonal elements of the MCHF operator. Koopman's theorem does not apply to MCHF calculations. The

values of A_0 are a measure of the behavior of the orbitals at the origin and are defined by

$$A_0(nl) = (P_{nl}(r)/r^{l+1})|_{r=0}, \quad (2)$$

where $P_{nl}(r) = rR_{nl}(r)$.

Since the orbitals not included in the ground configuration (excited orbitals) are obtained from the solution of the appropriate MCHF equations, they are completely unrelated to HF or other orbitals obtained for excited states. Thus, for example, we have calculated the total HF energy of the excited 3P state $1s^2 2s^2 3p^2$ to be -36.83375 a.u. and $\langle r \rangle_{3p} = 5.63$ a.u.; on the other hand, in the four-configuration calculations for the ground state of C the diagonal energy of the $1s^2 2s^2 3p^2$ configuration is -36.07851 a.u. and $\langle r \rangle_{3p} = 2.25$ a.u. In fact, the excited orbitals are always concentrated in the same region of space as the $2p$ orbital; this may be seen from the values of $\langle r \rangle$ given in Table II. The principal quantum number n of the orbitals serves only to distinguish different orbitals and refers to the number of radial nodes that the function has in the region where it is large. The inhomogeneities in the MCHF equations may introduce additional nodes into the radial functions⁹ but we have always found that the values of the functions are small in the region of these extra nodes.

III. DISCUSSION

As the $2p$ shell in carbon is unfilled, it is, as a first approximation, very tempting to suggest that the difficulty with the HF approximation in calculating the term values is that it does not take into account the *quasidegeneracy* which arises from the excitation $1s^2 2s^2 2p^2 \rightarrow 1s^2 2p^4$. Carbon is a particularly favorable case to

⁸ We use the term quasidegenerate because the two states are degenerate in the absence of the two electron interaction. See Ref. 5 for extensive calculations on such mixing for $2p$ shell atoms and ions.

⁹ D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A154**, 588 (1936); P. S. Bagus, Phys. Rev. **139**, A619 (1965). Although the origin of extra nodes is discussed with reference to Hartree-Fock one-configuration functions, the arguments are valid also for multiconfiguration functions.

study this point since all three states which arise from the p^2 configuration, namely, 3P , 1D , and 1S , also arise from the p^4 configuration.

From the results in Table I for the two-configuration wave functions, we see that the error for the $^3P-^1D$ transition hardly changes at all from the one configuration error, but the error for the $^3P-^1S$ transition is sharply reduced from 40% to less than 4%. Thus, the error in the ratio $(^3P-^1D)/(^1D-^1S)$ which was about 22% for the HF calculation (and which we would like to reduce to as close to zero as possible) has now become 73%.

Thus the quasidegeneracy of the $2s$ and $2p$ orbitals is not the answer to our problem. This could in fact be foreseen from very recent calculations of Froese¹⁰ on 0 , 0^+ , and 0^{2+} . She found that in 0 , for example, the error in the ratio $(^3P-^1D)/(^1D-^1S)$ was 30% using HF functions and was 28% using the two-configuration multiconfiguration calculation. In 0^{2+} an error of 30% is found in both calculations.

For the four- or five-configuration calculations the results in Table II show that the $^3P-^1D$ transition is hardly improved while the $^3P-^1S$ transition has now become much worse. The result is that the ratio $(^3P-^1D)/(^1D-^1S)$ is now in error by 230%.

The results from the three- and four-configuration give an error in the ratio $(^3P-^1D)/(^1D-^1S)$ which is 1.1%. These calculations then are those which give the best approximation to a constant error in the energy calculation for each state.

It may well be surprising to suggest using a configuration interaction function where the configuration which makes the largest contribution to the energy has been removed.

This may, however, be reasonable. Jucys¹¹ has pointed out that the method of multiconfiguration

calculation proposed by Hartree, Hartree, and Swirles² can be generalized even in the framework of restricted HF basis. [By the term restricted HF orbitals we mean that the orbitals are constrained to have the functional form of Eq. (1).] In their method there is only one orbital $P(nl, r)$ calculated for a given value of nl no matter how many different configurations contain nl . In a more general variational calculation nl would become nl' , nl'' , etc., and these functions would not be orthogonal. Jucys makes the point that the total symmetry of the pair of electrons that have been "excited" should be the same in the "ground" and "excited" states. Thus if one calculated the function $c_1|1s^22s^22p^2| + c_2|1s^22p'^22p^2|$, then one could ensure that $2p'^2$ has the 1S symmetry of $2s^2$. In other words you should "correct" occupied orbitals (in the HF scheme) by orbitals which do not appear in the HF scheme.

Since we are unable to compute the $2s^2 \rightarrow 2p'^2$ excitation using a nonorthogonal $2p'$ orbital, we choose to consider for the last set only excitations from the $2p^2$ shell of the ground-state configuration.

We need to have more experience and to examine the results for other p^2 configurations (as, for example, the ground-state configurations of Si and Ge) in order to discover whether we can obtain equally good results for the term splitting for other systems by restricting ourselves to excitations from the $2p^2$ shell.

Note added in proof. Our attention has been called to a paper by J. Hinze and C. C. J. Roothaan, *Progr. Theoret. Phys. (Kyoto)* **40**, 37 (1967). They have used an analytical expansion method to calculate MCHF functions for the 3P , 1D , and 1S states of carbon. Their results are very similar to those reported in this paper.

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¹⁰ C. Froese, *Proc. Phys. Soc. (London)* **90**, 39 (1967).

¹¹ A. P. Jucys, *Advan. Chem. Phys.* (to be published).