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Superposition of Configurations and Atomic Oscillator Strengths—Carbon I and II*

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Variational wave functions are computed for the ground state and a number of excited states of carbon I and II by the method of superposition of configurations. To accelerate convergence, the virtual orbitals are obtained from a pseudonatural orbital transformation on a single electron pair, out of all those possible within a given quantum shell. Expansions of up to 50 configurations are generated and used to study the effects of correlation on the oscillator strengths. The method appears to be fairly successful in correcting for most of the correlation error in both the energy and "correlation-sensitive" oscillator strengths. Term values are substantially improved over the Hartree-Fock values; and generally, although not always, f values appear to be obtainable with an accuracy of about 25%.

INTRODUCTION

THE calculation of atomic transition probabilities has traditionally been based on a single-configuration, independent-particle model.[1] In this approximation, the calculation reduces to the evaluation of a one-electron transition integral, corresponding to the transition of an electron from one single-particle state (orbital) to another. A variety of approximations have been used to obtain the orbitals, notable among them being the self-consistent field,[2] Thomas-Fermi,[3] and Coulomb approximations.[4] The model has generally proved quite successful, particularly for Rydberg transitions, as might be expected.

It has also been long realized that configuration interaction can have a drastic effect on such calculations,[1,5–7] and provision has always been made for a very limited amount of configuration mixing, as may be indicated by the structure of the spectrum. There have also been numerous investigations of the effects of "asymptotically degenerate configurations," i.e., the mixing of those configurations which would approach degeneracy in the large-Z limit of an isoelectronic series.[8–11] Here, too, only a very small number of configurations are normally considered.

However, the effect on the transition moment of the correlation error, which is inherent in the independent-particle model, has not been investigated too extensively. Although there are many ways to construct a better approximation to the exact wave function, probably the most generally useful one is the superposition of configurations (SOC) expansion. Here, the lead term is the traditional independent-particle wave function, and the succeeding terms *appear* to represent excitations of one or more electrons into excited orbitals. Since, however, these virtual configurations are used to represent the details of electron correlation, they will tend to emphasize those regions of space where the charge density is greatest and thus will usually bear little resemblance to "real" excited state configurations. While the kinds of configuration mixing mentioned in the preceding paragraph should be important, they must be considered to be only the first few terms in a SOC expansion.

In this paper, the method of superposition of configurations has been used to compute the correlation corrections to both the energies and oscillator strengths of neutral and singly ionized carbon. Such extensive SOC calculations have already yielded accurate f values for neutral helium[12] and, by incorporating part of the correlation into a polarization potential, also for neutral magnesium.[7] In a sense, the present calculations represent an extension of this work to a more correlation-sensitive situation.

A particularly interesting feature of these calculations is the use made of the pseudonatural orbital technique of Edmiston and Krauss[13] to generate a rapidly converging and variationally optimum set of virtual orbitals. This results in compressing most of the correlation effects into a relatively small number of configurations, although, ultimately, the SOC procedure remains slowly converging with respect to the final small bits and pieces of the correlation. One point to be kept in mind is the relative ease with which one

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can compute the bulk of the correlation effects since most of the computational labor simply involves getting the Hartree-Fock starting point. While this should be of considerable importance for molecules, it should be added that the difficulties arising from using very large basis sets will remain and could pose additional computational problems.

In the next section, to pinpoint the correlation-sensitive transitions, we will review briefly the current situation for some first row atoms. This will be followed by a description of the superposition of configurations method, with a fairly detailed account of the pseudonatural orbital technique and the way it has been applied here. Finally, the results will be presented and discussed for carbon I and II.

CORRELATION-SENSITIVE TRANSITIONS

A number of equivalent quantities can be used to characterize an atomic transition probability.[1] For theoretical purposes, the most convenient are probably the multiplet strength

$$S_{ij}=|\langle\Phi_i|\mathbf{r}|\Phi_j\rangle|^2, \qquad (1)$$

and the oscillator strength

$$f_{ij}=\tfrac{2}{3}\Delta E_{ij}g_i^{-1}S_{ij}. \qquad (2)$$

Here, i and j refer to the initial and final terms of the transition, respectively, ΔE is the energy difference in atomic units,[14] and g_i is the statistical weight of the initial term. One can also use the formally equivalent dipole velocity form[15,16]

$$S_{ij}=(\Delta E_{ij})^{-2}|\langle\Phi_i|\nabla|\Phi_j\rangle|^2, \qquad (3)$$

which must agree with the dipole length form (1) for the exact wave function, but need not do so if approximate wave functions are used. It is also supposed that the squared transition moments in (1) and (3) are summed over all degeneracies in the initial and final states.

In all these formulas, Φ_i and Φ_j refer to the full many-electron eigenfunctions for the atom. In the independent-particle model, with the wave functions for both states assumed to be antisymmetrized products of one-electron functions (orbitals), the multiplet strength assumes the particularly simple form

$$S_{ij}=\mathcal{S}\sigma^2, \qquad (4)$$

where σ is the transition integral

$$\sigma=(4l_>^2-1)^{-1/2}\int_0^\infty dr\,P_i(r)rP_j(r). \qquad (5)$$

P_i and P_j are the orbital radial functions for the jumping electron, and $\mathcal{S}$ is a numerical factor depending on the number of equivalent electrons, angular momenta, etc. Equation (4) depends on the simplifying assumption that only one orbital changes in the transition. If core-relaxation effects are taken into account, S is somewhat complicated by the introduction of overlap integrals and exchange terms, although, in general, (4) will still represent the dominant feature.

Since electron correlation refers to the detailed effects on the wave function of the interelectronic interactions, the independent-particle model should represent a rather severe approximation for those transitions involving a number of equivalent, or "shell-equivalent," electrons. The prime suspect, for first-row atoms, are transitions of the type

$$2s^22p^n\text{-}2s2p^{n+1},$$

where the $2s$ and $2p$ electrons mutually interpenetrate each other quite strongly. In view of the fairly substantial core penetration of $3s$ electrons, the transitions,

$$2p^n\text{-}2p^{n-1}3s,$$

might also be sensitive to correlation corrections.

This correlation sensitivity is illustrated by Table I, where calculations for a selection of transitions are compared with measurements. The emission experiments were carried out either with a wall-stabilized arc[17,18] or a shock tube,[19] and they should have uncertainties in the 30% range. The lifetime experiments, for the most part, were done by the phase-shift method,[20] although there is some very recent data obtained with the foil excitation technique using accelerators.[21] In both cases, the accuracy should be around 10–15%. For nitrogen and oxygen, the Hartree-Fock f values have been calculated using the Hartree-Fock[2] σ^2 and the observed wavelengths. Thus, these numbers differ slightly from those of Kelly, who used the theoretical energy interval in Eq. (2). The Z-expansion calculations are first-order approximations to the Hartree-Fock combined, where possible, with the configuration mixing

$$2s^22p^n+2p^{n+2}.$$

It thus represents the first obvious step in a multiconfiguration expansion and should include some portion of the correlation correction.

Several observations can be made on the material in this table. Firstly, these kinds of transitions tend to lie well into the ultraviolet, thus increasing the difficulties of experimental work. Indeed, all the measurements are of quite recent vintage. While the $2p$-$3s$ transitions tend to fare somewhat better, the comparisons are generally far from satisfactory; the errors range from

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[14] Atomic units are used throughout this paper; the unit of length is the Bohr radius, $a_0=0.52917$ Å, and energy is measured in units of $2R_m$, the appropriate reduced-mass rybderg.

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TABLE I. A comparison of calculated and measured oscillator strengths for some first-row atoms and ions.

Atom	Transition	Wavelength (Å)	Calculated Hartree-Fock[a]	Calculated Z-exp.[b]	Measured Emission[c]	Measured Lifetime[d]
B I	$2s^22p\,{}^2P-2s2p^2\,{}^2D$	2089		0.253		0.048
C I	$2s^22p^2\,{}^3P-2s2p^3\,{}^3D$	1561	0.286	0.232	0.091	0.076
	$-2s2p^3\,{}^3P$	1329	0.202	0.256	0.039	
	$-2s^22p3s\,{}^3P$	1657	0.075		0.17	0.13
C II	$2s^22p\,{}^2P-2s2p^2\,{}^2D$	1335	0.274	0.204		0.114
	$2s2p^2\,{}^2P-2p^3\,{}^2D$	2512	0.228	0.230	0.136	
N I	$2s^22p^3\,{}^4S-2s2p^4\,{}^4P$	1134	0.491	0.515	0.137	0.080
	$2p^3\,{}^2D-2p^23s\,{}^2D$	1243	0.062		0.110	0.095
	$-2p^23s\,{}^2P$	1492	0.048		0.111	0.078
	$2p^3\,{}^2P-2p^23s\,{}^2P$	1742	0.049		0.093	0.064
	$2p^3\,{}^4S-2p^23s\,{}^4P$	1200	0.099		0.350	0.259
N II	$2s^22p^2\,{}^3P-2s2p^3\,{}^3D$	1085	0.240	0.192		0.109
	$-2s2p^3\,{}^3P$	916	0.172	0.213		0.131
	$-2s2p^3\,{}^3S$	645	0.323	0.244		0.189
	$-2s^22p3s\,{}^3P$	672	0.089			0.067
O I	$2p^4\,{}^3P-2p^33s\,{}^3S$	1302	0.030			0.035

[a] For nitrogen and oxygen, see Kelly (Ref. 2). The boron and carbon results have been obtained here.
[b] See Cohen and Dalgarno (Ref. 10).
[c] The emission data for C I are from Boldt (Ref. 17), and for N I from Labuhn (Ref. 18). Those for C II are from Roberts and Eckerle (Ref. 19).
[d] Except for N II, all the lifetime data are taken from Lawrence and Savage (Ref. 20). N II includes results obtained by Heroux (Ref. 21).

50% to a factor of 5. A few generalizations are suggested, namely, that the $2s$-$2p$ transitions seem to be too large, while the $2p$-$3s$ are too small, although there are a few exceptions to these rules. Furthermore, the very limited configuration mixing of the Z-expansion calculations does not seem to be doing too much good; sometimes the results are improved, sometimes they are not.

Figure 1 probably indicates the real source of the difficulty. Here, the Hartree-Fock $2s$ and $2p$ orbitals and the length and velocity transition integrands [Eq. (5)] are plotted for the $2s^22p^2$-$2s2p^3$ transition in carbon—the transition integrands being plotted in arbitrary units. It is clear that the tails of the wave functions are irrelevant for determining the transition moment, whose integrand is largest where the electronic charge density is largest. It is thus to be expected that calculations of oscillator strengths for these transitions are apt to be plagued by all the ills arising from correlation errors.

SUPERPOSITION OF CONFIGURATIONS AND PSEUDONATURAL ORBITALS

The procedure adopted here for incorporating correlation corrections into the wave function has been the method of superposition of configurations (SOC), where a variational trial function is written as a linear combination of known many-electron functions

$$\Psi=\sum_i a_i\Phi_i. \tag{6}$$

The configurations Φ_i are themselves antisymmetrized products of orbitals, and the coefficients a_i are determined by the requirement that the energy integral be an extremum

$$E=\langle\Psi|\mathcal{H}|\Psi\rangle/\langle\Psi|\Psi\rangle. \tag{7}$$

The Hamiltonian used here is the usual nonrelativistic, spin-independent Hamiltonian

$$\mathcal{H}=\sum_i(-\Delta_i/2-Zr_i^{-1})+\sum_{i>j}r_{ij}^{-1}, \tag{8}$$

where Z is the nuclear charge. The variational principle leads to the usual matrix eigenvalue equation for the energy and the coefficients a_i. The eigenvalues are always upper bounds to the energy of the corresponding excited (or ground) state,[22] and, with a physically appropriate trial function (6), the computed wave func-

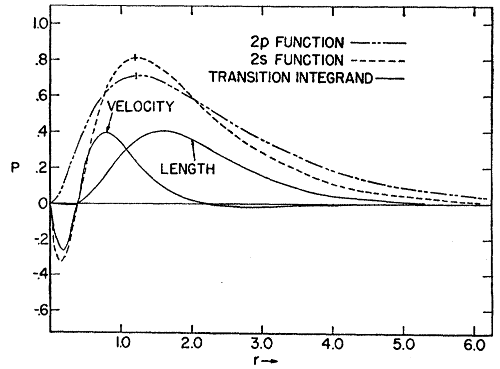

FIG. 1. Hartree-Fock radial functions compared with length and velocity transition integrands for a $2s^22p^2-2s2p^3$ transition in carbon.

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[22] J. K. L. MacDonald, Phys. Rev. 43, 830 (1933).

tion is an approximation to the eigenfunction of that state.

It is furthermore supposed that the traditional Hartree-Fock approximation will be a suitable starting point for the calculations, i.e., the first, and usually dominant, term of (6) is taken as the Hartree-Fock function of the state under investigation. For a closed-shell system, the Hartree-Fock wave function is the variationally best single determinant of orbitals φ_i:

$$\Psi=\det\varphi_1\alpha(1)\varphi_1\beta(2)\varphi_2\alpha(3)\cdots\varphi_n\beta(2n)\,, \tag{9}$$

where α and β are the $\pm\frac{1}{2}$ component spin functions. In the more general open-shell case, (9) becomes a linear combination of determinants such that the spin and orbital angular momenta add up to produce a pure state in LS coupling; the orbitals are populated strictly in accordance with the *aufbau* principle. The particular version of the Hartree-Fock scheme which is used here is the expansion method developed by Roothaan and co-workers.[23] In this form of the theory, the orbitals are expanded in a (truncated) set of analytical basis functions

$$\varphi_i=\sum_p c_{ip}\chi_p\,, \tag{10}$$

where the c_{ip} are variationally determined to give, in effect, a "best fit" to the Hartree-Fock orbitals. In particular, the basis functions used were the Slater-type orbitals (STO's)

$$\chi_{nlm}=(2\zeta)^{n+1/2}[(2n)!]^{-1/2}r^{n+1}e^{-\zeta r}Y_l^m(\vartheta,\varphi)\,. \tag{11}$$

The ζ's are additional variational parameters which usually turn out to have values which sprinkle the basis functions radially throughout those regions of space where the Hartree-Fock orbitals are significantly large. For the ground state of carbon, for instance, the s basis (for *both* $1s$ and $2s$) consists of five functions, two of which span the K-shell loop, two the L-shell loop, and one the intermediate region.

To return to the SOC expansion (6), the particular form that it now takes is

$$\Psi=a_0\Phi_0+\sum_{n,i}a_n^i\Phi_n^i+\sum_{n,i}\sum_{m,j}a_{nm}^{ij}\Phi_{nm}^{ij}+\cdots\,, \tag{12}$$

where Φ_0 is the Hartree-Fock function, and the notation Φ_n^i means to replace the nth-occupied (space) orbital of Φ_0 by some virtual orbital φ_i, taking the necessary linear combination of determinants to give a pure LS state. Similarly, Φ_{mn}^{ij} are the double substitution terms. In principle, the sums should run over all the occupied orbitals and a complete set of virtual orbitals, and the expansion should extend on through triple substitutions, etc. In practice, of course, the sums are truncated to a relatively few terms, and usually only single and double substitutions are included, i.e., only the pair correlations are treated.[24] Furthermore, since the spectroscopy is the main interest here, only excitations of the "optical" electrons are considered, i.e., for carbon the K shell is left alone as a Hartree-Fock $1s^2$ pair.

The crux of the problem then is how to optimize the choice of the virtual orbitals φ_i. The procedure adopted here is the pseudonatural orbital (PSNO) transformation of Edmiston and Krauss,[13] which is a simple extension of the natural orbital theory of Löwdin,[25] as applied to a two-electron system.[26] Since this scheme not only appears to work quite well but is also exceedingly easy to use, we will give a fairly detailed account of it here.

The procedure can be outlined briefly as follows. To begin with, an ordinary SOC calculation is done, correlating only one of the electron pairs in (12). The virtual orbitals are constructed by arbitrarily Schmidt orthogonalizing the analytical Hartree-Fock basis functions (11), with perhaps some additional STO's whose ζ's have been optimized for this calculation. A natural orbital transformation is then carried out to generate a new set of virtual orbitals, which also concentrates most of the correlation information of (12) into just a few terms. This set of orbitals is then taken as the virtual orbitals for other substitutions of physically similar pairs of electrons.

As the two-electron prototype, let us consider a doubly occupied singlet, such as the $1s^2\ {}^1S$ ground state of helium. A SOC calculation which utilizes *all* possible combinations of orbitals from some given orthonormal set $[\varphi_i]$ then gives a wave function of the form

$$\Psi(1,2)=\sum_n C_{nn}\varphi_n(1)\varphi_n(2)+\sum_{n>l}C_{nl}\times2^{-1/2}[\varphi_n(1)\varphi_l(2)+\varphi_n(2)\varphi_l(1)]\,. \tag{13}$$

The first-order density matrix is given by

$$\rho(1'|1)=\int dV_2\bar{\Psi}(1',2)\Psi(1,2)=\sum_{nl}\bar{\varphi}_n(1')\varphi_l(1)\gamma_{nl}\,, \tag{14}$$

where the $\boldsymbol{\gamma}$ matrix is

$$\boldsymbol{\gamma}=\mathbf{C}\mathbf{C}^{\dagger}\,. \tag{15}$$

$\mathbf{C}$ is simply the symmetric matrix of the SOC coefficients in (13). The unitary matrix which diagonalizes $\mathbf{C}$ also diagonalizes $\boldsymbol{\gamma}$ and can be used to transform the orbital set $[\varphi_i]$ to a new orthonormal set $[\psi_i]$, such that both the first-order density matrix and the wave function are quadratic forms

$$\Psi(1,2)=\sum_n a_n\psi_n(1)\psi_n(2)\,, \tag{13$'$}$$

$$\rho(1'1)=\sum_n a_n^2\bar{\psi}_n(1')\psi_n(1)\,. \tag{14$'$}$$

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The orbitals $[\psi_n]$ are called the *natural orbitals*, and they represent the most rapidly converging set which can be constructed from the original orbital set. The squared coefficients a_n^2 are the *occupation numbers*, and they serve to order the orbitals in order of importance in (13′). It should be noted that, in one sense, nothing new has been achieved, since the wave function (13′) is identical with the original one (13). What has been accomplished is to compress the information in the original expansion into its most compact possible form. Also, while there are some technical modifications, there is no inherent difficulty in extending the theory to excited states,[26] such as triplets or mixed orbital symmetries, e.g., $(1s2p)$.

The Edmiston-Krauss adaptation for more than two electrons will now be illustrated for the ground state of carbon, $2s^22p^2\,{}^3P$, one of the cases actually calculated in this paper. Here, an orthonormal set of virtual orbitals is constructed by successively Schmidt orthogonalizing the Hartree-Fock basis functions χ_i [Eq. (11)] to themselves and the occupied Hartree-Fock orbitals $(1s,2s,2p)$, with the addition of some d and f functions;

$$[\varphi_i]=1s,2s,3s',4s',\cdots,2p,3p',4p',\cdots,3d'\cdots. \quad (16)$$

This set is then used in a full (6-electron) SOC calculation on the carbon atom, but concentrating on just one pair of electrons, namely, the $2s2p\,{}^1P$ pair, i.e., the wave function analogous to (13) is

$$\Psi=(2s2p)^3P(2s2p+2s3p'+3s'2p+3s'3p'+\cdots 2p3d'+3p'3d'+\cdots)^1P. \quad (17)$$

All possible combinations of the virtual orbitals were used, and, wherever the basis was augmented, the ζ's of the additional functions were varied to minimize the total energy. At this point the coefficients from (17) are treated exactly as though they came from a genuine two-electron SOC calculation, and the coefficient matrix is diagonalized to determine a *pseudo*natural orbital (PSNO) transformation

$$[1s,2s,3s',4s',\cdots 2p,3p',4p',\cdots 3d']\rightarrow [1s,2s,3s,\cdots 2p,3p,\cdots 3d].$$

In a sense, what one is doing is determining the natural orbitals for the $2s2p\,{}^1P$ pair in the Hartree-Fock field of the rest of the atom. Upon repeating the calculation with the PSNO's, it was found that, to within 0.01 eV, 8 or 9 configurations yielded the same energy as the original 41 configurations of (17); i.e., there is a similar compression of information as in the true two-electron case.

The next step is to observe that, since the $2s$ and $2p$ are so strongly interpenetrating, these PSNO's should also be very nearly the appropriate virtual orbitals for any other pair excitations of the outer four electrons, e.g., excitations from $2s^2$, $2p^2$, etc. Using these PSNO's then, other groups of configurations are added onto the wave function in a routine search for the energetically important terms, until all single and double substitution possibilities have been exhausted. It should be noted here that the Hartree-Fock functions are retained for the $2s$ and $2p$ orbitals, with the PSNO's orthogonalized to them. The basic philosophy is that this pseudonatural orbital transformation is simply a technique for mechanically determining an approximately optimum set of virtual orbitals for representing the correlations of the outer four electrons. The ordering of the PSNO's, $3s$, $4s$, etc., follows the occupation numbers of the transformation and hence should represent their order of importance.

Detailed results for the ground state of carbon are shown in Table II, where energies are given for two distinct sequences of wave functions. The first sequence is obtained by adding onto the Hartree-Fock successive groups of configurations which are presumed to represent different pair correlations, e.g., $2p^2$ correlation, etc. ΔE is the correlation energy picked up by adding the corresponding group, and ΔE_{sum} is the running sum

TABLE II. Superposition of configurations energies (in au) for the ground state of carbon, $2s^22p^2\,{}^3P$.

No. of Terms	Configurations	$-E_{\text{tot}}$	ΔE	ΔE_{sum}
1	$2s^22p^2$	37.68861	···	···
6	$2s^2(2p^2+3p^2+4p^2+3d^2+4d^2+4f^2)$	37.69808	0.0095	0.0095
18	6-conf.$+(3s^2+4s^2+3p^2+3d^2+4d^2)2p^2+2p^3({}^4S+{}^2D+{}^2P)(3p+4p)$	37.72495	0.0269	0.0363
25	18-conf.$+(2s2p)^3P(3s3p+4s4p+3p3d+4p3d+3p4d+3d4f+4d5f)^1P$	37.74142	0.0165	0.0528
29	25-conf.$+(2s2p)^1P(3s3p+3p3d+4p3d+3p4d)^3P$	37.74361	0.0022	0.0550
34	29-conf.$+(2s2p)^3P(3s3p+4s4p+3p3d+4p3d+3p4d)^3P$	37.74637	0.0028	0.0578
35	34-conf.$+(2s3s)^3S(2p^2)^3P$	37.74795	0.0016	0.0593
36	35-conf.$+(2s3d)^3D(2p^2)^3P$	37.76127	0.0133	0.0727
37	36-conf.$+(2s3d)^3D(2p^2)^1D$	37.77833	0.0171	0.0897
40	37-conf.$+3p^2({}^3P+{}^1D)(2p^2)^3P+(2p^3)^2D4f$	37.77888	0.0006	0.0903
1	$2s^22p^2$	37.68861	···	···
2	$(n=2)2s^22p^2+2p^4$	37.70582	0.0172	0.0172
21	$(n=3)$	37.77053	0.0647	0.0819
39	$(n=4)$	37.77851	0.0080	0.0899
40	$(n=5)$	37.77888	0.0004	0.0903

TABLE III. Superposition of configurations energies (in au) for the $2s^22p^2\,{}^1S$ state of carbon.

No. of Terms	Configurations	$-E_{\rm tot}$	ΔE	$\Delta E_{\rm sum}$
1	$2s^22p^2$	37.54961	...	...
11	$2s^2(2p^2+3p^2+2p4p+4p^2+5p^2+3d^2+4d^2+5d^2+4f^2+5f^2+3s^2)$	37.59038	0.0408	0.0408
18	11-conf.$+(3s^2+4s^2+2p^2+3p^2+3d^2)2p^2+2p^3(3p+4p)$	37.65325	0.0629	0.1036
27	18-conf.$+(2s2p){}^1P(3s3p+3s4p+4s4p+3p3d+3p4d+4p3d+4p5d+3d4f+4d4f){}^1P$	37.67276	0.0195	0.1232
32	27-conf.$+(2s2p){}^3P(3s3p+4s4p+3p3d+3p4d+4p3d){}^3P$	37.67708	0.0043	0.1275
35	32-conf.$+(2s3d+2s4d+3s4d){}^1D(2p^2){}^1D$	37.67805	0.0010	0.1284
37	35-conf.$+(3p^2){}^3P(2p^2){}^3P+(3p^2){}^1D(2p^2){}^1D$	37.67930	0.0013	0.1297
1	$2s^22p^2$	37.54961	...	...
2	$(n=2)2s^22p^2+2p^4$	37.60813	0.0585	0.0585
16	$(n=3)$	37.66390	0.0558	0.1143
32	$(n=4)$	37.67789	0.0140	0.1283
37	$(n=5)$	37.67930	0.0014	0.1297

As might be expected, the parallel spin $2p^2$ pair has a small correlation energy ($\simeq$0.25 eV), and, in agreement with Kelly's[27] results for oxygen, the $2s^2$ correlation energy is rather large ($\simeq$0.7 eV). The 36 and 37 configuration results are particularly interesting, since the added configurations do not fit too readily into any particular correlation breakdown but are still quite important. These configurations represent the excitation of a single $2s$ electron to make a $2s3d\,{}^3D$ pair, with all the angular momenta subsequently recoupled to give a ${}^3P$ state for all four-electrons. They apparently correspond to a spin-polarization type of correlation effect. These two configurations account for about 0.8 eV of the total four-electron correlation energy of 2.4 eV, and such triplet coupled terms have turned out to be important in other states and systems. For instance, in the $2p^2\,{}^1D$ state, the single configuration $(2s3d\,{}^3D)(2p^2\,{}^3P)$ contributes 0.85 eV to the correlation energy. To test the additivity of pair-correlation energies, calculations were also done with each group of configurations alone being added to the Hartree-Fock, i.e., without any of the other pair correlations. While the sum of *these* correlation-energy increments did not add up exactly to the directly computed four-electron correlation energy, the difference was no greater than 0.2 eV.

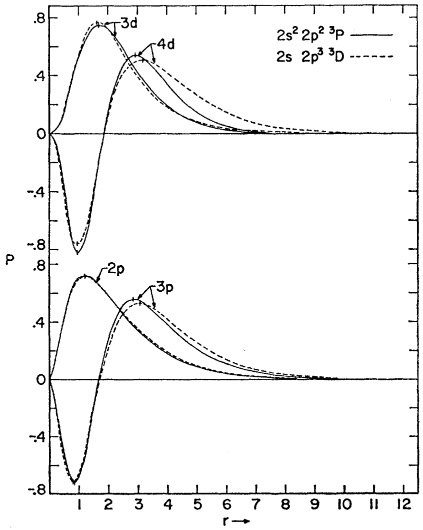

FIG. 2. Radial functions of Hartree-Fock ($2p$) and pseudonatural ($3p$, $3d$, and $4d$) orbitals for the $2p^2\,{}^3P$ and $2s2p^3\,{}^3D$ terms of neutral carbon.

The second set of calculations in Table II utilizes the same 40 configurations listed in the first part of the table. Here, however, a sequence of wave functions is constructed by successively adding onto the Hartree-Fock all those configurations containing the $n=2$ orbitals ($2s$ and $2p$), then all those with the $n=3$ orbitals ($3s$, $3p$, and $3d$), etc., with the quantum numbers defined by the ordering of the pseudonatural orbital occupation numbers. Thus, this represents a sequence of progressively longer expansions and, hopefully, better approximations to the exact wave function, and they are the functions that will be used in computing the spectroscopic properties.

To illustrate some of the similarities and dissimilarities in correlation behavior in going from state to state, the corresponding results for the $2p^2\,{}^1S$ state are given in Table III. Both the $2p^2$ and $2s^2$ correlation energies are much larger here, the former, no doubt, because of the parallel spin, double occupancy of the $2p$ orbitals. The large $2s^2$ correlation apparently reflects a much stronger mixing of the $2p^4$ configuration. The total double-excitation intershell effects appear to be about the same, 0.022 a.u. for the ${}^3P$ and 0.024 a.u. for the ${}^1S$. However, the $2s\rightarrow 3d$ apparent single excitations are quite unimportant for the ${}^1S$ state.

Several tests were made to check out the procedure of using PSNO's from one pair to represent the other pair correlations. The ground-state calculations were repeated using p, d, and f functions derived from the $2p^2$ pair and s functions from the $2s^2$ pair. With these orbitals, a 38-configuration calculation gave a computed correlation energy for the ground state of 0.0889 a.u., 0.04 eV higher than the result reported in Table II. It should be added here that this calculation utilized an analytical STO basis consisting of five s and four p func-

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[27] H. P. Kelly, Phys. Rev. 144, 39 (1966).

tions (the Hartree-Fock basis) plus three d and two f functions, whereas the Table II results were obtained by augmenting the s and p bases by one function each. Another check is shown in Fig. 2, where some of the principal PSNO's from the $2p^2\,{}^3P$ ground state are compared with the corresponding orbitals for the $2s2p^3\,{}^3D$ excited state. In the latter case the orbitals were derived from a SOC calculation on the $2p^2\,{}^1D$ pair, i.e., in this case, the original SOC calculation corresponding to (17) was of the form

$$\Psi=(2s2p)^3P(2p^2+2p3p+3p^2+\cdots 3d^2+3d4d+\cdots 2s3d+3s3d+\cdots)^1D. \quad (18)$$

The similarity of the PSNO's is quite striking, especially when one recalls that they were derived not only from different pairs, but also from different electronic states of the atom. As is to be expected, all the orbitals tend to be concentrated in those regions of space with the greatest charge density. Thus, the "pseudoquantum numbers," $3p$, $3d$, etc., have little, if anything, to do with the corresponding quantum numbers of real excited states. This is illustrated in Fig. 3, where the Hartree-Fock $3d$ function for the $2p3d$ (center of gravity) excited state is compared with the $3d$ PSNO for the ground state. The variationally optimum $3d$ function for a SOC expansion of the ground state is radically different from the "true" excited state orbital; in fact its radial dependence is very nearly the same as that of the $2p$ function.

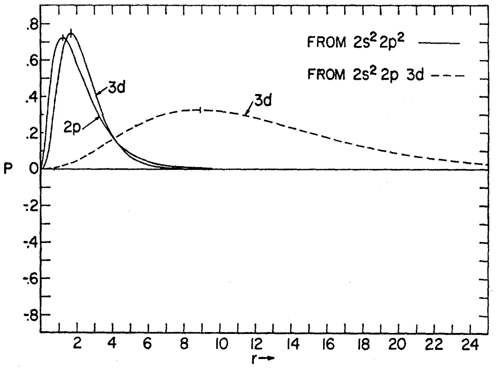

FIG. 3. Radial functions for the ground state and a $2p3d$ excited state of neutral carbon.

TERM VALUES AND OSCILLATOR STRENGTHS FOR CARBON I

The term values for a number of low-lying states computed in this way are shown in Table IV and compared with the spectroscopic data.[28] The different columns in this table correspond exactly to the second sequence of wave functions shown in Tables II and III. Each of the excited states is treated variationally and completely independently of all the others; i.e., parameters are varied, configurations selected, etc. to depress each total energy as much as seems feasible. The computed term scheme in Table IV is an *after the fact* representation of the way these total energies are settling into place relative to each other as progressively longer expansion lengths are used in the trial functions. It seems clear that, in general, there is reasonably good agreement ($\simeq$300 cm^{-1}) between the calculated and measured term values, especially considering the fact that these are completely *ab initio* total energy calculations. The sole exception is the $2s2p^3\,{}^3P$ term, which is off by about 1900 cm^{-1}. This is not the lowest state of its symmetry, the $2p3s\,{}^3P$ being lower, so that here one has to work with the second eigenvalue in the secular equation. It appears to be necessary to include a number of configurations which represent the $2p3s$ "inner loop" of the $2s2p^3$ as well as the pair correlations proper, and this has simply not been carried far enough here. The SOC expansion lengths ranged from 37 configurations for the $2p^2\,{}^1S$ to 50 for both terms of $2s2p^3$.

TABLE IV. Relative term energies (in au) for neutral carbon.

Term		H-F	$n=2$	$n=3$	$n=4$	$n=5$	Observed[a]
$2s^22p^2$	^3P	0.0	0.0	0.0	0.0	0.0	0.0
	^1D	0.0573	0.0579	0.0539	0.0480	0.0478	0.0463
	^1S	0.1390	0.0977	0.1066	0.1006	0.0996	0.0985
$2s^22p3s$	^3P	0.2662	0.2436	0.2773	0.2771	0.2764	0.2750
	^1P	0.2720	0.2487	0.2840	0.2829	0.2821	0.2823
$2s2p^3$	^3D	0.2943	0.2871	0.2993	0.2944	0.2936	0.2919
	^3P	0.3509	0.3687	0.3640	0.3527	0.3513	0.3428

[a] See Ref. 28.

A few comments about the $2p^2$ term spacings may be pertinent at this point. Adding only the $2p^4$ configuration brings the ^1S term into position relative to the ground state, although it does not improve the ^1D (see the $n=2$ column of Table IV). However, omitting $2p^4$ and including only the $2p^2$ correlation configurations (the second line of Tables II and III) yields 0.0494 and 0.1077 au for the ^1D and ^1S terms, respectively, which is also reasonably satisfactory. Thus the final computed term values appear to represent a rather subtle interplay of a number of correlation effects.

The oscillator strengths, in both the length and velocity forms, are shown in Table V, with exactly the same format as the term values, i.e., as a sequence of presumably better approximations. While the degree of convergence is not completely satisfactory, the average of the length and velocity values for the last column ($n=5$) is usually within about 25% of the correct value. The sole exception is the transition involving the $2s2p^3\,{}^3P$, whose computed term value was so far out of line. Since the lifetime experiment measures a total transition probability for the decay from $2p3s\,{}^1P$, it only provides an upper limit for the transition to $2p^2\,{}^1D$, the

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[28] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. (U. S.) Circ. No. 467 (U. S. Government Printing Office, Washington, D. C., 1949), Vol. 1.

Table V. Absorption oscillator strengths for neutral carbon.

Transition	λ(Å)	Type	H-F	Computed $n=2$	$n=3$	$n=4$	$n=5$	Observed Arc[a]	Lifetime[b]
$2s^22p^2\,{}^3P-2s2p^3\,{}^3D$	1561	Len.	0.286	0.204	0.131	0.122	0.102	0.091	0.076
		Vel.	0.332	0.432	0.175	0.149	0.117		
$2s^22p^2\,{}^3P-2s2p^3\,{}^3P$	1329	Len.	0.202	0.260	0.131	0.121	0.097	0.039	
		Vel.	0.171	0.120	0.161	0.136	0.105		
$2s^22p^2\,{}^3P-2s^22p3s\,{}^3P$	1657	Len.	0.075	0.075	0.105	0.108	0.108	0.17	0.13
		Vel.	0.094	0.094	0.123	0.124	0.123		
$2s^22p^2\,{}^1D-2s^22p3s\,{}^1P$	1931	Len.	0.079	0.080	0.092	0.092	0.092		<0.101
		Vel.	0.084	0.085	0.106	0.109	0.108		
$2s^22p^2\,{}^1S-2s^22p3s\,{}^1P$	2478	Len.	0.097	0.097	0.091	0.081	0.081		
		Vel.	0.098	0.092	0.101	0.095	0.090		

[a] See Ref. 17. [b] See Ref. 20.

other decay mode being to $2p^2\,{}^1S$. If the final calculated f values are used to determine the $2p3s\,{}^1P$ lifetime, one obtains 3.30 and 2.82 nsec for length and velocity, respectively, while the measured lifetime is 2.9±0.3 nsec.

A number of shorter expansions were also calculated utilizing only the few most important configurations, as indicated by the energy improvement and the size of the coefficients. The kind of result one obtains for the oscillator strength is illustrated in Table VI for the $2s^22p^2\,{}^3P$-$2s2p^3\,{}^3D$ transition. While it is clear that one can find a two-configuration approximation for both states which gives a good f value, the addition of a few terms, just as important energetically, has the disappointing effect of making matters worse. By the time all the $n=3$ configurations have been added (Table V), the f values have changed substantially for the worse. Although it would be eminently desirable to identify just a few configurations important for the oscillator strength, it does not yet seem clear, from these results, how to go about it.

TERM VALUES AND OSCILLATOR STRENGTHS FOR CARBON II

Superposition of configuration wave functions, of about the same accuracy and utilizing the PSNO transformation technique, were also computed for the ground state and a number of excited states of singly ionized carbon. While there have recently been lifetime[20] and shock-tube[19] measurements of some C II f values, there are a number of transitions for which very accurate experimental data are lacking. C II also has the interesting feature that some of the transitions are quasi-forbidden in an independent-particle model but can become allowed by configuration mixing. These are multiplets of the $2s^23p$-$2s2p^2$ transition array.

A detailed breakdown of the calculations for the $2s^22p\,{}^2P$ ground state is given in Table VII, exactly analogous to the neutral case. It should be noted here that for C$^+$ the analytical basis sets were not refined quite as much as for the neutral atom. For instance, for the ground state, the basis was only augmented by the addition of new symmetries (d and f functions), i.e., the basis consisted of five s, four p, three d, and one f function. The PSNO's for the ground state were derived from the $2s2p\,{}^1P$ pair. Here, the $2s3d$, spin-polarization type of term appears as the two configurations

$$(2p3d\,{}^1P)2s \quad\text{and}\quad (2p3d\,{}^3P)2s.$$

These two configurations account for about 0.6 eV of the computed correlation energy of 2.17 eV. The ionization energy computed from C and C$^+$ ground states is 11.06 eV, while the experimental value is 11.26 eV. The difference of 0.2 eV can easily arise from the K-L intershell correlation, as well as the accumulated slow

Table VI. Some "small wave function" calculations of the $2s^22p^2\,{}^3P-2s2p^3\,{}^3D$ oscillator strength.

$2s^22p^2\,{}^3P \downarrow$ \ $2s2p^3\,{}^3D \rightarrow$		$2s2p^3$	$2s2p^3+2s^22p3d$	$2s2p^3+2s^22p3d+3d2p^3$	3-conf.$+2s2p\,{}^3P3p^2\,{}^1D+2s3p{}^1P2p^2\,{}^3P$
$2s^22p^2$	l.	0.286	0.154	0.155	0.172
	v.	0.332	0.039	0.041	0.078
$2s^22p^2+2p^4$	l.	0.204	0.097	0.104	0.118
	v.	0.432	0.079	0.097	0.151
$2s^22p^2+2p^4$ $+2s3d{}^3D(2p^2\,{}^3P+{}^1D)$	l.	0.177	0.087	0.092	0.105
	v.	0.525	0.114	0.133	0.195
Observed: (Arc) 0.091					
(Lifetime) 0.076					

TABLE VII. Superposition of configurations energies (in au) for C II, $2s^22p\ ^2P$.

No. of Terms	Configurations	$-E_{\mathrm{tot}}$	ΔE	ΔE_{sum}
1	$2s^22p$	37.29222	...	...
7	$(2s^2+3s^2+2p^2+3p^2+3d^2+4d^2+4f^2)2s$	37.33705	0.0448	0.0448
15	$7\text{-conf.}+2p^2(^1S+^3P+^1D)(3p+4p)+3p^2(^3P+^1D)2p$	37.33954	0.0025	0.0473
25	$15\text{-conf.}+(3s2p+3s3p+3s4p+4s4p+2p3d+3p3d+4p3d+3p4d+3d4f+4d4f)^1P2s$	37.36561	0.0261	0.0734
34	$25\text{-conf.}+(3s2p+3s3p+3s4p+4s4p+2p3d+3p3d+4p3d+3p4d+3d4f)^3P2s$	37.37215	0.0065	0.0799
35	$34\text{-conf.}+2p^24f$	37.37241	0.0003	0.0801
1	$2s^22p$	37.29222	...	...
2	$(n=2)2s^22p+2p^3$	37.33270	0.0405	0.0405
18	$(n=3)$	37.36730	0.0346	0.0751
35	$(n=4)$	37.37241	0.0051	0.0801

convergence errors of the SOC approximation. The K-L intershell correlation energy for beryllium has been calculated to be approximately 0.14 eV.[29]

The computed term values are given in Table VIII, in exactly the same form as for neutral carbon. Here too, for each state individually, a sequence of wave functions is computed which, variationally at least, represents a progressively better approximation. The overall results tend to be somewhat more coarse than for C I, with errors generally in the 500–1000 cm^{-1} range. This, no doubt, is due to the less refined basis sets, as well as K-L intershell effects, aggravated by the higher stage of ionization. Some recent separated pair calculations on the Be sequence indicate that the intershell correlation energy increases with increasing charge.[30] Also, Hartree-Fock calculations on the lithium isoelectronic sequence[31] give errors in the term values, which increase with Z. On the whole, the term scheme has been brought into pretty good shape, as is indicated by Fig. 4. which displays the information of Table VIII on an energy-level diagram.

The calculated oscillator strengths are collected together in Table IX and compared with the available experimental data. The ^2S states exhibit a very strong mixing of the two configurations

$$2s2p^2+2s^23s\,.$$

This gives two dominant components to the transition moment, and the mixing occurs in such a way that they very nearly cancel each other for the $2s^22p$-$2s^23s$ transition, which is thus both weak and numerically unreliable. This mixing also makes allowed the quasiforbidden transition

$$2s2p^2\ ^2S\text{-}2s^23p\ ^2P\,,$$

and, indeed, the calculated f value agrees quite satisfactorily with the experimental one. This effect actually does not show up in Table IX until the $n=4$ column, because of a fortuitous labeling of the PSNO's such that the 4s PSNO is the one that looks like the spectroscopic 3s. The other quasiforbidden transitions, $2s2p^2$-$2s^23p$ and $2s^23d$-$2p^3$, remain essentially forbidden even with

TABLE VIII. Relative term energies (in au) for C II.

Term		H-F	$n=2$	$n=3$	$n=4$	$n=5$	Observed[a]
$2s^22p$	^2P	0.0	0.0	0.0	0.0	0.0	0.0
$2s2p^2$	^4P	0.1313	0.1717	0.1901	0.1941		0.1959
	^2D	0.3285	0.3690	0.3487	0.3447	0.3443	0.3412
	^2S	0.4270	0.4675	0.4611	0.4454	0.4446	0.4395
	^2P	0.5115	0.5520	0.5146	0.5102		0.5040
$2s^23s$	^2S	0.5233	0.5360	0.5358	0.5381	0.5346	0.5308
$2s^23p$	^2P	0.5994	0.5740	0.5973	0.6003		0.6001
$2p^3$	^4S	0.5953	0.6358	0.6449	0.6477		0.6469
$2s^23d$	^2D	0.6553	0.6392	0.6696	0.6692	0.6691	0.6630
$2p^3$	^2D	0.6969	0.7374	0.6912	0.6895	0.6889	0.6854

[a] See Ref. 28.

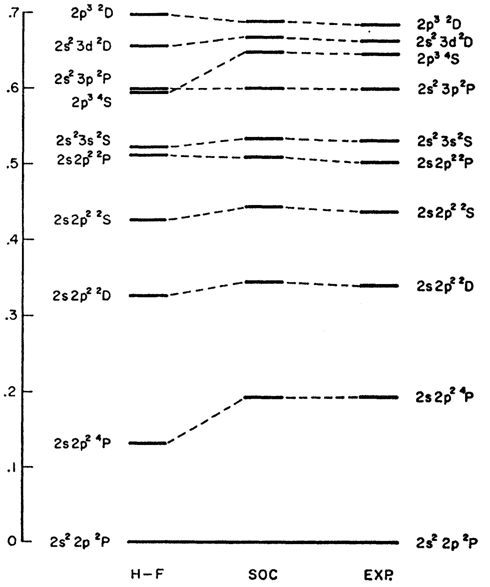

FIG. 4. The energy levels (in au) for carbon II as given by Hartree-Fock (H-F) and superposition of configurations (SOC) calculations, and compared with the observed (Expt).

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[29] H. P. Kelly, Phys. Rev. **131**, 684 (1963).

[30] K. Miller (private communication).

[31] A. W. Weiss, Astrophys. J. **138**, 1262 (1963).

TABLE IX. Absorption oscillator strengths for C II. The transitions marked with an asterisk (*) are subject to large uncertainties, as discussed in the text.

Transition	λ(Å)	Type	Computed					Observed
			H-F	$n=2$	$n=3$	$n=4$	$n=5$	
$2s^22p\,^2P-2s2p^2\,^2D$	1335	l.	0.274	0.186	0.122	0.121	0.121	0.114[a]
		v.	0.256	0.325	0.116	0.124	0.124	
$-2s2p^2\,^2S$	1037	l.	0.072	0.117	0.094	0.119	0.119	
		v.	0.042	0.020	0.111	0.129	0.130	
$-2s2p^2\,^2P$	904	l.	0.726	0.489	0.502	0.510		
		v.	0.302	0.377	0.512	0.518		
* $-2s^23s\,^2S$	858	l.	0.043	0.013	0.002	0.003	0.008	
		v.	0.050	0.005	0.003	0.004	0.010	
$-2s^23d\,^2D$	687	l.	0.276	0.356	0.351	0.330	0.330	
		v.	0.245	0.284	0.328	0.307	0.307	
*$2s2p^2\,^2D-2s^23p\,^2P$	1760	l.	0.0	0.0	0.007	0.009	0.009	
		v.	0.0	0.0	0.019	0.016	0.016	
$-2p^3\,^2D$	1324	l.	0.245	···	0.145	0.138	0.138	
		v.	0.232	···	0.140	0.135	0.136	
$2s2p^2\,^2S-2s^23p\,^2P$	2837	l.	0.0	0.001	0.002	0.127	0.127	0.133[b]
		v.	0.001	0.012	0.054	0.129	0.137	
*$2s2p^2\,^2P-2s^23p\,^2P$	4741	l.	0.0	0.0	0.0	0.0		
		v.	0.001	0.0	0.0	0.0		
$-2p^3\,^2D$	2512	l.	0.228	···	0.104	0.101	0.101	0.136[b]
		v.	0.627	···	0.085	0.091	0.092	
$2s^23s\,^2S-2s^23p\,^2P$	6575	l.	0.901	0.439	0.631	0.640	0.702	
		v.	1.031	0.270	0.619	0.668	0.758	
$2s^23p\,^2P-2s^23d\,^2D$	7244	l.	0.645	0.604	0.577	0.569	0.568	
		v.	0.531	0.422	0.425	0.562	0.562	
*$2s^23d\,^2D-2p^3\,^2D$	20342	l.	0.0	0.0	0.0	0.0	0.0	
		v.	0.0	0.058	0.005	0.002	0.002	
$2s2p^2\,^4P-2p^3\,^4S$	1010	l.	0.207	···	0.175	0.175		
		v.	0.121	···	0.193	0.191		

[a] See Ref. 20.
[b] See Ref. 19.

the extended wave functions used here, and they probably are, in fact, quite weak. While there is often a substantial change in the f value in going from the Hartree-Fock to the most elaborate calculation, it is gratifying to note that this is not the case, or at least not very drastic, for the classic Rydberg transitions ($2p$-$3d$,$3s$-$3p$,$3p$-$3d$). On the whole, it does not seem too unreasonable to suggest that the mean of the final length and velocity values is probably accurate to within about 25%. This appears to be consistent with the available experimental data as well as with whatever trends may be evident in the calculations.

DISCUSSION

In summary, it appears that an independent-particle model is likely to be inadequate for treating those transitions which intimately involve a number of equivalent, or "shell-equivalent," electrons, the correlation-sensitive transitions. The correlation corrections have been included here by using variational, superposition of configurations wave functions, taking the Hartree-Fock approximation as the starting point. The main feature of the calculations, which makes intermediate range accuracy so readily attainable on present day computers, has been the use of a pseudonatural orbital transformation on some representative electron pair to generate an ordered set of nearly optimum virtual orbitals. This technique is closely related to the multiconfiguration, or extended Hartree-Fock procedure,[32–34] which sets up a mathematical formalism for determining *all* the orbitals self-consistently in the field generated by a many-configuration trial function. The core is thus allowed to relax in the field of the correlating electrons, which is not the case here. Carried to comparable lengths, however, the two schemes should be very nearly identical. The present scheme also appears to be very similar to a recently developed procedure based on solving the symmetry adapted Bethe-Goldstone equations.[35]

As for the results, it appears that this SOC-PSNO procedure rapidly recovers a large portion of the correlation energy, although it will still be subject to difficulties of slow convergence when very high accuracy (10 cm^{-1} or better) is wanted. It is relatively easy, however, to include a large enough portion of the correlation corrections to yield useful and significant results. Ionization and excitation energies appear to be computable with an accuracy comparable to the Hartree-Fock for alkali-like atoms (0.1–0.2 eV), which is good enough for many purposes. It seems that oscillator strengths are also obtainable at this level of accuracy, namely, approximately 25%, although some care may be needed in assessing the reliability of an individual f value. Needless to say, a 25% accuracy for f values is generally quite satisfactory,[36] being of the same order of accuracy of most present day experimental techniques. When combined with the procedure of always using a systematically generated sequence of functions, instead of an isolated wave function calculation, this technique should prove to be a valuable complement to the present experimental work on atomic f values.

ACKNOWLEDGMENTS

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