

Theory of atomic structures including electron correlation. V. Excited states not lowest of their symmetry and oscillator strengths in neutral and singly ionized atoms*

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The non-closed-shell many-electron theory (NCMET) of Sinanoğlu is applied to excited states which are not the lowest of their symmetry. Variational collapse towards lower states of the same symmetry is prevented by use of the Hylleraas-Undheim-MacDonald theorem. The procedure for calculating such states is described. Using it, variationally correct charge wave functions are obtained and for the first time for several $2s2p^n$ excited states in neutral and singly ionized atoms of carbon, nitrogen, oxygen, and fluorine. The configuration labels of these states and lower energy states of the same symmetry are found in agreement with the experimentally assigned orderings in each case. Optical oscillator strengths are calculated with these wave functions and are found in good agreement with experiment where previous calculations in the literature had shown large discrepancies.

I. INTRODUCTION

A new atomic structure theory which includes all of the correlation effects in both ground and excited states has recently been developed by Sinanoğlu.¹ In this theory, a non-closed-shell atomic or molecular state is shown to contain rigorously three types of electron correlation beyond the Hartree-Fock wave function (RHF wave function, ϕ_{RHF}): (i) "internal" (χ_{INT}); (ii) "semi-internal" (including orbital polarizations) (χ_{F}); and (iii) the closed-shell-like "all-external" correlations (χ_{U}).

In the closed-shell limit (like the Ne ground state), the first two specifically non-closed-shell-type correlation effects vanish. Only the last "all-external" correlations remain; and these, as shown first in the earlier closed-shell many-electron theory of Sinanoğlu (MET),² are made up mainly of pair correlations ($\{\hat{u}_{ij}\}$).

Sinanoğlu showed in the *non-closed-shell* generalization of his MET, which we refer to as NCMET¹ (non-closed-shell many-electron theory), that electronic charge distributions $\rho(\vec{r})$ and the resulting "chargelike properties," like electronic quadrupole moments, hyperfine constants, form factors, also transition densities $\rho_{on}(\vec{r})$, and the resulting oscillator strengths, etc., should be given to high accuracy just from what he called the "charge distribution wave function ψ_{CD} ," or the "charge wave function ψ_c " for short. This $\psi_c = \phi_{\text{RHF}} + \chi_{\text{INT}} + \chi_{\text{F}}$ contains rigorously only a finite number of determinants or configurations which are the ones that constitute the internal and semi-internal correlations in their entirety.

The present series of papers³⁻⁶ by Sinanoğlu and co-workers have been applying the new electronic structure theory to the accurate determin-

ation of various atomic properties both to test and demonstrate the theory by comparison with experiments and to provide atomic data, especially where such data could not be obtained reliably from methods like RHF before.

In papers I and II,^{3,4} the energies of charge wave functions were calculated for well over a hundred states of configurations $1s^2 2s^n 2p^m$ for isoelectronic sequences. All-external pair-correlation energies $\epsilon_{ij,kl}$ too were deduced and applied to term splittings, ionization potentials, and electron affinities. In paper III, Sinanoğlu and Westhaus calculated dozens of in-shell $2s^n 2p^m \rightarrow 2s^{n-1} 2p^{m+1}$ -type transitions, predicting many new oscillator strengths f^{E1} which have agreed, within the experimental error of a few percent, with experimental results, some obtained before, some after the theoretical results became available. The new experiments involve the beam-foil (BFS), phase-shift, etc., type of new measurement techniques. By contrast, previous theoretical methods had often disagreed by factors of, say, 2-3. In IV,⁶ we provided forbidden lifetimes which are otherwise very difficult to measure. The charge wave function and properties calculations were carried out by fully automated program systems (ATOM) developed by Sinanoğlu, Öksüz, Westhaus, and Luken.

The ψ_c 's and f^{E1} 's of *M*-shell ($3s^n 3p^m 3d^k$) states, which are considerably larger in their numbers of determinants, have also been obtained⁷; the f^{E1} 's in atoms like Mg, Si, P, and Cl agreeing with new BFS data well, while previous methods like RHF differed by factors as large as 10-30.

In previous applications of NCMET, nearly all of the states involved have been the lowest of their symmetry.³⁻⁷ The *L*-shell states of +2 and higher + ξ ions, for example, are of this type. In

using the variation method for the ψ_c , one then just minimizes the lowest root of the Hamiltonian matrix for a given symmetry.

Many neutral and +1 ion L -shell states, however, are not the lowest of their symmetry. Then subtleties of variational theory for higher states come in. Sinanoğlu's NCMET and the automated program system ATOM should also work for such "nonlowest" states. However, in doing this, it is necessary to make sure that the correct roots of the secular equation corresponding to the desired states are picked out. Some recent calculations⁸ on such states have yielded oscillator strengths showing serious discrepancies with experiment. It has been noted by Hibbert,⁹ however, that these calculations involve variational collapse resulting from selection of incorrect roots of the secular equation.

In the present paper, we classify the atomic and molecular states with respect to their "lowest" and "nonlowest" aspects. We then show how variational theory can be correctly applied to calculate the NCMET charge wave functions ψ_c for nonlowest states. The paper is on such practical aspects. NCMET itself is unchanged, being just the same for lower or upper states of either type. The calculations were carried out using ATOM.

Variationally correct NCMET charge wave functions ψ_c 's were then calculated here for the first time for several $2s2p^n$ states in neutral and singly ionized carbon, nitrogen, oxygen, and fluorine atoms. In each case the calculated configuration assignments of these states and their lower-lying states of the same symmetry are found in agreement with the experimentally assigned orderings. In addition, f^{E1} values that we calculate with these wave functions are found to be in good agreement with experiment, resolving the discrepancies⁸ encountered earlier.⁹ The new nonlowest-state NCMET wave functions have also been used to obtain¹⁰ the first fully non-closed-shell correlated generalized oscillator strengths $F_{on}(\vec{q})$ and integrated inelastic electron scattering cross sections $\sigma_{on}(E)$ for Be, B, C, N, and O showing large differences (factors of 2–10) from the Hartree-Fock results.

The nonlowest NCMET states problem treated in this paper occurs often also in molecules. The excited-state potential energy curves,¹¹ molecular-electron impact spectra, etc., calculations with NCMET will then involve the considerations given here also.

II. FOUR TYPES OF ELECTRONIC STATES IN ATOMS AND MOLECULES

The classification scheme below is based on two criteria: The first is simply the number (e.g.,

zero, finite, or infinite) of lower states of the same symmetry. The second is based on the relationship of the configuration label of the state of interest to those of the lower-lying states of the same symmetry. This relationship depends upon what we call a "vertical substitution." A vertical substitution is defined as the replacement of one orbital in an N -electron configuration with another orbital to produce a new configuration which, based strictly on qualitative arguments (e.g., nodal planes, core penetration, etc.) and without specific detailed calculations, is unambiguously higher in energy than the initial configuration.

In atoms, a vertical excitation is determined by the replacement of orbital nl (principal quantum number n , angular momentum l) with an orbital $n'l'$ such that $n' \geq n$, $l' \geq l$, and $n'l' \neq nl$. For example, this includes the replacement of a $2s$ with a $3s$ or a $2p$ orbital, as in the conversion of the $1s^2 2s^2$ configuration to the $1s^2 2s 3s$ or the $1s^2 2s 2p$ configuration. Specifically excluded are the reverse processes (e.g., substitution of $2s$ for $2p$) and ambiguous substitutions such as $3d \rightarrow 4s$ in which n increases as l decreases or vice versa.

In molecules, vertical substitutions include the replacement of molecular orbital $n\gamma$ with molecular orbital $n'\gamma$, where $n' > n$ and γ is an irreducible representation of the molecular point group, for example $3a_g \rightarrow 4a_g$ in D_{2h} ethylene. Other substitutions such as $\pi \rightarrow \pi^*$, etc., where a bonding orbital is replaced by an antibonding orbital or a nonbonding orbital, may also be included.

Type 1: Lowest states of a symmetry. This category includes all states with the lowest energy of their symmetry, such as all actual ground states, all $1s^2 2s^2 2p^m$ states, etc. Most $2s 2p^m$ states also fall into this category. A list of the more important exceptions is given in Table I.

Type 2: "Vertical upper states." A state is of type 2 if there are a finite (nonzero) number of lower states of the same symmetry, and the configuration label of the state can be formed from each of those of the lower states by making only vertical substitutions. This includes, for example, the $1s^2 2s^2 9p^2 P^o$ of the boron atom. This state lies above the $1s^2 2s^2 n p^2 P^o$, $n = 2-8$, and it is related to each by an $np \rightarrow 9p$ ($n < 9$) substitution. Another example is the $1s^2 2p^2 1S$ state in the boron +1, carbon +2, etc., positive ions. In each case, this state lies above the $1s^2 2s^2 1S$ state, which is related by two $2s \rightarrow 2p$ substitutions, as illustrated in Fig. 1(a).

Type 3: "Nonvertical upper states." This category includes all states which lie above a finite (nonzero) number of lower states of the same symmetry, and which are not of type 2. Two

TABLE I. L -shell states not lowest of their symmetry. This list includes all L - S coupled terms belonging to $2s2p^m$ and $2s^02p^2$ configurations which do not have the lowest energy for their symmetry in neutral atoms and positive ions.

Configuration ($1s^2 + \dots$)	L - S term (Symmetry)	Atomic number(s)	Number of lower states ^a	Variational type ^b	Configuration(s) of lower state(s) ($1s^22s^2 + \dots$)
$2s2p^2$	2S	$Z=5$	4	3	$3s, 4s, 5s, 6s$
$2s2p^3$	$^3P^o$	$Z=6$	1	3	$2p3s$
$2s2p^3$	$^1D^o, ^1P^o$	$Z=6$	∞	4	$2pnd, n=3-\infty$
$2s2p^3$	$^1P^o$	$Z=7$	1	3	$2p3s$
$2s2p^4$	4P	$Z=7$	1	3	$2p^23s$
$2s2p^4$	$^2D, ^2S, ^2P$	$Z=7$	∞	4	$2p^2nd, n=3-\infty$
$2s2p^4$	2P	$Z=8$	1	3	$2p^23s$
$2s2p^5$	$^3P^o$	$Z=8$	2	3	$2p^33s, 3d$
$2s2p^5$	$^1P^o$	$Z=8$	∞	4	$2p^3nd, n=3-\infty$
$2s2p^5$	$^1P^o$	$Z=9$	1	3	$2p^33s$
$2s2p^6$	2S	$Z=9$	∞	4	$2p^4nd, n=3-\infty$
					($1s^2 + \dots$)
$2p^2$	1S	$Z=4$	∞	4	$2sns, n=2-\infty$
$2p^2$	1S	$Z \geq 5$	1	2	$2s^2$

^a Based on experimental observations (Ref. 17).

^b See text.

such cases are illustrated in Figs. 1(b) and 1(c). In Fig. 1(b), both states are related to an intermediate configuration by vertical substitutions. However, both substitutions lead away from the intermediate state and it is not possible to convert one state into the other making only vertical excitations. The three states in Fig. 1(c) are related only by the nonvertical substitution $3d \rightarrow 4s$. In scandium, $3d4s^2$ is lowest; in titanium (+1), $3d^24s$ is lowest; and in vanadium (+2), $3d^3$ is lowest. Another example of such a state is the $2s2p^4^4P$ in the nitrogen atom. This state lies above the $2s^22p^23s^4P$ which is related to it by a $2s \rightarrow 2p$ (vertical) substitution and a $3s \rightarrow 2p$ (non-vertical) substitution. Several additional examples

of such states are given in Table I.

Type 4: States in the continuum. This category contains all states which lie above an infinite number of states of the same symmetry. In general, these states will lie above an infinite number of discrete states, usually in the form of a Rydberg series terminating at an ionization limit. In addition there will also be a continuous distribution of continuum states with energies below, adjacent to, and above the state of interest. In some cases there are several Rydberg series, ionization limits, and continua involved. Several examples of type-4 states are given in Table I. The $1s^22p^2^1S$ in the beryllium atom, for example, lies above the $1s^22sns^1S$ ($n \geq 2$) series.

III. VARIATIONAL CALCULATION OF NCMET CHARGE WAVE FUNCTIONS

Type-1 states: For type-1 states, the familiar ground-state variational principle applies. The lowest root of the charge wave function Hamiltonian matrix is minimized. Examples of such calculations on states belonging to L -shell configurations have been given previously.^{1,4} Without changing any of the theoretical considerations involved, we refined the computational details of this process further. The most important of these refinements is the use of two semi-internal orbitals of d symmetry, instead of only one, and separate optimization of each semi-internal orbital (i.e., $\hat{f}_s, \hat{f}_p, \hat{f}_d, \hat{f}_d'$, and \hat{f}_f) instead of using the single variational parameter approximation described previously.⁴ For these (type-1) states, however, the results of the current refined calcu-

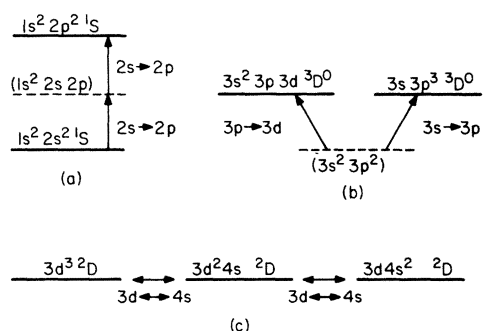


FIG. 1. Vertical and nonvertical upper states. (a) A vertical upper state, the $2p^2^1S$ state in boron +1, carbon +2, etc., positive ions, which is related to the lower lying $2s^2^1S$ by two $2s \rightarrow 2p$ substitutions. (b) and (c) Nonvertical upper states. The two $^3D^o$ states in (b) are related by two opposing substitutions. The three states in (c) are related by $3d \leftrightarrow 4s$ nonvertical substitutions.

lations differ little from the results obtained previously.^{4,5}

For states not of type 1, the "lowest state" variational principle does not apply and other methods are required. The most useful approach to states not lowest of their symmetry is the Hylleraas-Undheim-MacDonald (HUM) theorem.¹²⁻¹⁴ As shown by Hylleraas and Undheim¹² and MacDonald,¹³ each eigenvalue $E_{\gamma_i}^{(M)}$ for $i=0$ to $M-1$ of the matrix $H_{\gamma}^{(M)}$ and its associated wave function $\Psi_{\gamma_i}^{(M)}$ are variationally bounded by the correspondingly ordered eigenvalue E_{γ_i} and eigenfunction Ψ_{γ_i} of the exact Hamiltonian H_{Γ} . Therefore, in order to calculate a variational wave function for the third state of ${}^3P^o$ symmetry of the oxygen atom, for example, it is necessary to minimize the third eigenvalue of a matrix representation of the oxygen atom Hamiltonian using a basis of three or more configurations each of ${}^3P^o$ symmetry.

The key to application of the HUM method is selection of the correct eigenvalue of the Hamiltonian matrix. The ordering of the chosen eigenvalue must correspond exactly to the ordering of the exact eigenvalue of the state of interest. In particular, selection of an eigenvalue does not depend in any way on the basis set used to construct the matrix. However, the basis set must be chosen to include the configuration labels not only of the state of interest but of all lower-lying states of the same symmetry. That is, the basis set must include at least the configuration of the state of interest plus explicit (i.e., linearly independent) representations of every lower state of the same symmetry. This may cause difficulties in molecular calculations because the configurational assignments and orderings are frequently unknown and may change with geometry. There are few such problems in atoms, however, the doubly excited helium, etc., spectra being interesting exceptions treated recently by other methods.¹⁵ As a rule, if there is any doubt about the position of a particular configuration (relative to the state of interest), it should also be included in the basis set because, even if it does not fall below the state of interest, it is likely to be important for reasons of near degeneracy.

Type-2 states: Application of the HUM method to type-2 states is especially easy because the ordering and separation of the lower states relative to the state of interest are characteristically insensitive to the choice of the orbitals used to construct the configurational basis functions. For example, in the case of the $1s^2 2p^2 {}^1S$ configuration in the positive ions B^+ , C^{+2} , etc., the only lower configuration of the same (i.e., 1S) symmetry is the $1s^2 2s^2 {}^1S$. This configuration, however, forms

the internal part of the NCMET charge wave function of the $1s^2 2p^2 {}^1S$ state, and it is automatically included (independent of variational considerations) in the basis set used to calculate the $1s^2 2p^2 {}^1S$ charge wave function. In addition, any physically reasonable choice of $1s$, $2s$ and $2p$ radial functions (e.g., shielded hydrogenic or, better, RHF) will yield correctly ordered $1s^2 2s^2 {}^1S$ and $1s^2 2p^2 {}^1S$ basis functions. The variational calculation of the charge wave function for this state, therefore, is performed exactly as described for type-1 states,^{1,4} except that the second 1S eigenvalue of the Hamiltonian matrix is minimized instead of the lowest one.

NCMET charge wave functions for the $1s^2 2p^2 {}^1S$ configuration of several ions have been calculated previously by this method. As in the cases of type-1 states, NCMET f values calculated using these charge wave functions¹⁶ are in good agreement with the recent accurate experimental results, unlike the corresponding RHF f values. Note, however, that the beryllium atom $1s^2 2p^2 {}^1S$ is not of type 2. It is specifically excluded from the current discussion.

Type-3 states: Application of the HUM method to type-3 states is more difficult than for type 2 because the positions of the lower configurations relative to the one of interest are very sensitive to details of the orbitals used to construct them. Physically reasonable orbitals, including even the RHF orbitals of the configuration of interest, can reverse the order of some configurations in these cases. Examples of this will be given in Sec. IV.

Characteristic difficulties in type-3 states are caused by orbitals which represent the configuration of interest better than lower-lying configurations. Such orbitals have the effect of elevating the lower configurations relative to the one of interest. The RHF orbitals of the configuration of interest can be a particularly poor choice because they minimize the energy of the configuration of interest, but not that of any of the lower configurations. The combined effects of lowering the upper configuration, while raising the lower configurations, can seriously diminish the separation between these configurations and even reverse their ordering.

In the nitrogen atom, for example, the $1s^2 2s 2p^4 {}^4P$ and the $1s^2 2s^2 2p^3 3s {}^4P$ are the two lowest configurations of 4P symmetry. The RHF wave functions of these configurations have energies of 11.23 and 10.03 eV, respectively, relative to the energy of the $1s^2 2s^2 2p^3 {}^4S^o$ RHF wave function. For comparison, the experimental term energies of the two lowest 4P states in nitrogen are 10.93 eV and 10.33 eV, respectively.¹⁷ The $1s$, $2s$, and $2p$ orbitals of the $1s^2 2s 2p^4 {}^4P$ wave func-

tions, however, differ slightly from those of the $1s^2 2s^2 2p^2 3s^4 P$ RHF wave function. If the $1s$, $2s$, and $2p$ orbitals determined by the $2p^2 3s$ RHF wave function are used to construct both configurations, the $2p^2 3s$ energy remains at 10.03 eV, but the $2s 2p^4$ energy rises to 13.66 eV, tripling the separation between the configurations. Alternatively, if the $1s$, $2s$, and $2p$ orbitals from the $2s 2p^4$ RHF wave function are used for both configurations, the $2p^4$ energy returns to 11.23 eV and the $2p^2 3s$ energy rises to roughly 11.2 eV or higher depending on the choice of the $3s$ orbital. For either choice of orbitals, the interaction between these configurations, i.e., $H_{12} = \langle 1s^2 2s 2p^4 4P | H | 1s^2 2s^2 2p^2 3s^4 P \rangle$, is roughly 0.3–0.4 eV. Therefore, if a 2×2 configuration interaction (CI) is performed using the $2p^2 3s$ orbitals, the results will indicate two widely separated, weakly interacting configurations. On the other hand, if the orbitals from the $2p^4$ are used, a 2×2 CI will indicate two strongly interacting, nearly degenerate configurations which mix in almost a 50/50 ratio. This example, which is typical of many cases, demonstrates that two very similar sets of orbitals can lead to completely opposite descriptions of the same states.

In order to overcome the above problem, we have found it useful to “minimize lowest states first.” That is, basis functions (configurations) which represent lower-lying states should be chosen to minimize their own energies before the upper state itself is treated. In particular, any orbital occupied in the upper configuration and/or any lower configuration should be taken from the RHF wave function of the *lowest* configuration in which it is found and not necessarily from the RHF wave function of the (upper) configuration of interest. Examples of this procedure are given in Sec. IV of this paper. By keeping the lowest configurations as low as possible, this method prevents upper and lower configurations from becoming accidentally degenerate or reversed in order because of the use of poor representations (with arbitrarily elevated energies) of the lower configurations.

NCMET charge wave functions of type-3 states have not been previously calculated in a variationally correct manner. The correct method for calculating such states will be demonstrated in Sec. IV of this paper on several $2s 2p^n$ states in this category.

Type-4 states: In the form considered here, the HUM method requires an infinite number of basis functions and diagonalization of a matrix of infinite dimension. Alternative techniques exist for the treatment of these cases^{18,19}; however, such methods will not be treated here.

IV. NCMET CHARGE WAVE FUNCTIONS FOR $2s 2p^n$ STATES NOT LOWEST OF THEIR SYMMETRY

In neutral atoms and positive ions, nearly all $2s 2p^n$ states are the lowest of their symmetry. Such states are of type 1 and the method for calculating charge wave functions of such states has been given previously.^{1,4} As shown in Table I, there are exactly fourteen $2s 2p^n$ cases which are not of type 1. Of these exceptions, all of which occur in neutral and singly ionized atoms, seven are type-3 states and seven are type 4. In this section we will apply the HUM method to calculate variationally correct charge wave functions for six of the seven type-3 states for the first time. These cases, in particular, are the carbon atom $2s 2p^3 3P^o$, the nitrogen +1 ion $2s 2p^3 1P^o$, the nitrogen atom $2s 2p^4 4P$, the oxygen +1 ion $2s 2p^4 2P$, the oxygen atom $2s 2p^5 3P^o$, and the fluorine +1 ion $2s 2p^5 1P^o$.

Nitrogen atom $2s 2p^4 4P$: The $2s 2p^4 4P$ state of the nitrogen atom, for example, is the second state of $4P$ symmetry in this atom, lying 0.6 eV above the $2s^2 2p^2 3s^4 P$ state.¹⁷ As indicated by NCMET,^{1,4} the charge wave function for the $2s 2p^4 4P$ state includes the configurations $2s^2 2p^2 \hat{f}_s$, $2s^2 2p^2 \hat{f}_d$, $2s 2p^3 \hat{f}_p$, $2s 2p^3 \hat{f}_f$, $2p^4 \hat{f}_s$, and $2p^4 \hat{f}_d$, where \hat{f}_s , \hat{f}_p , \hat{f}_d , and \hat{f}_f are semi-internal orbitals of s , p , d , and f symmetries, respectively, and each semi-internal orbital is orthogonal to all $1s$, $2s$, and $2p$ orbitals. In addition to these configurations, the variational (HUM) treatment of this state requires an explicit (i.e., linearly independent) representation of the lower-lying $2s^2 2p^2 3s$ configuration. This is obtained from the $2s^2 2p^2 \hat{f}_s$ configuration by splitting the \hat{f}_s semi-internal orbital into two parts given by

$$\hat{f}_s(\vec{r}) = 3s(\vec{r}) + \hat{f}'_s(\vec{r}), \quad \langle 3s | \hat{f}'_s \rangle = 0.$$

In our calculations the \hat{f}_d semi-internal orbital was also split into two parts,

$$\hat{f}_d(\vec{r}) = 3d(\vec{r}) + \hat{f}'_d(\vec{r}), \quad \langle 3d | \hat{f}'_d \rangle = 0,$$

in order to represent the $2s^2 2p^2 3d 4P$ configuration. This configuration is not necessarily required in this case because it lies above the $2s 2p^4 4P$. However, it was included in the current calculations to take care of any near degeneracy effects which might arise from the relatively small separation (2 eV) between the $2s 2p^4 4P$ and the $2s^2 2p^2 3s d 4P$ configurations.

The resulting set of configurations are listed in the first column of Table II. Variational trial wave functions for the $2s 2p^4$ charge wave function are obtained by calculating the matrix of the nitrogen atom Hamiltonian using this set of configurations as a basis set. In this case, because the

TABLE II. The NCMET charge wave function for the $2s2p^4^4P$ state of the nitrogen atom, $^4P(1)$ and the lower-lying $^4P(0)$ state as calculated in this work, and the results of previous calculations. Correlation normalization^a is used for all cases except the $^4P(0)$ wave function of this work (third column), which is normalized to unity.

Configuration ($1s^2 + \dots + ^4P$)	Configurational coefficient			
	This work— $^4P(1)^b$	NCMET $^4P(0)^b$	Previous calculations $^4P(0)^c$	Previous calculations $^4P(0)^d$
$2s2p^4$	1.0000	0.5056	1.0000	1.0000
$2s^22p^23s$	0.7123	-0.8261
$2s^22p^2\hat{f}'_s$	0.0290	-0.0555
$2s^22p^2\hat{f}_s$	-0.0558	-0.3586
$2s^22p^23d$	0.1116	0.0202
$2s^22p^2\hat{f}'_d$	0.2076	0.0870
$2s^22p^2\hat{f}_d$	0.2104	0.2003
$2s2p^3\hat{f}_p(1)^e$	0.4193	0.1743	...	-0.1187
$2s2p^3\hat{f}_p(2, 3, 4)^e$	0.0924	0.0682	0.0389	0.0759
$2s2p^3\hat{f}_f$	0.0219	0.0120	0.0128	0.0225
$2p^43s$	-0.0915	0.1204
$2p^4\hat{f}'_s$	0.0281	0.0220
$2p^4\hat{f}_s$	0.0403
$2p^43d$	-0.0165	-0.0045
$2p^4\hat{f}'_d$	-0.0544	0.0270
$2p^4\hat{f}_d$	-0.0545	-0.0515
Orbital	Semi-internal STO exponential factor ^f			
\hat{f}'_s or \hat{f}_s	1.991(3s)	1.991(3s)	1.600(3s)	0.849(3s)
\hat{f}_p	0.900(2p)	0.900(2p)	1.600(3p)	1.079(3p)
\hat{f}_d or \hat{f}'_d	1.626(3d)	1.626(3d)	1.600(3d)	1.279(3d), 2.558(3d)
\hat{f}_f	2.813(4f)	2.813(4f)	0.960(4f)	2.813(4f)

^a That is, $\Psi = \Phi_{\text{RHF}} + \chi$, where $\langle \Phi_{\text{RHF}} | \Phi_{\text{RHF}} \rangle = 1$ and $\langle \Phi_{\text{RHF}} | \chi \rangle = 0$.

^b $1s$, $2s$, $2p$, and $3s$ radial functions taken from $1s^22s^22p^23s^4P$ RHF wave function.

^c $1s$, $2s$, and $2p$ radial functions taken from $1s^22s2p^4^4P$ RHF wave function. In this work the exponential factors were restricted to $\xi_{3s} = \xi_{3p} = \xi_{3d} = (5/3)\xi_{4f}$ to prevent variational collapse, and no further variation was attempted. See Ref. 4 (Paper I).

^d $1s$, $2s$, and $2p$ radial functions taken from $1s^22s2p^4^4P$ RHF wave function. See Ref. 8(b). The roots of the matrix minimized by these authors led to partial variational collapse rather than approximating the state desired.

^e There are four distinct $2s2p^3\hat{f}_p$ 4P terms. These have been divided into one term containing only single orbital excitations from the $2s2p^4$ determinant and three others containing all other excitations (e.g., $2p2p' \rightarrow 2p''\hat{f}_p$). For brevity the coefficients of these last three terms have been combined together into a single coefficient.

^f These are the exponential factors α_{nl} used in each of the STO's, $r^n \exp(-\alpha_{nl}r)Y_{lm}$, to represent the semi-internal orbitals in each calculation. The nl values of each STO are given in parentheses after each α_{nl} . The \hat{f}_d orbital in the right-hand column contained two STO's.

$2s2p^4^4P$ is the second-lowest state of 4P symmetry, the variational trial wave function is determined by minimizing the eigenvalue of the second-lowest 4P eigenvector of this matrix (and not the lowest ones as found in type-1 cases).

To calculate a particular trial wave function,

the radial parts of each of the orbitals ($1s$, $2s$, $2p$, $3s$, $3d$, \hat{f}'_s , \hat{f}_p , \hat{f}'_d , \hat{f}_f) must be specified. Following the rule "minimize lowest states first," the $1s$, $2s$, $2p$, and $3s$ radial functions were each taken from the RHF wave function of the $1s^22s^22p^23s^4P$ configuration (and not, as in type-1

cases,² from the $1s^2 2s 2p^4 {}^4P$ RHF wave function), because this choice minimizes the energy of the $1s^2 2s^2 2p^2 3s {}^4P$ configuration. A hydrogenic $3d$ radial function $r^2 \exp(-r/3)$ was used for the $3d$ orbital, because this choice is a very good approximation to the RHF $3d$ radial function in the $1s^2 2s^2 2p^2 3d {}^4P$ RHF wave function.²⁰ Each of the semi-internal orbitals (i.e., \hat{f}'_s , \hat{f}'_p , \hat{f}'_d , and \hat{f}'_f) was approximated with a single Slater-type orbital [STO $-r^n \exp(-\alpha_n r) Y_{lm}$] Schmidt orthogonalized to the $1s$, $2s$, $2p$, $3s$, and $3d$ orbitals.

With this choice of $1s$, $2s$, and $2p$ radial functions (i.e., from the $1s^2 2s^2 2p^2 3s {}^4P$ RHF wave function) the $1s^2 2s 2p^4 {}^4P$ is no longer represented with its own RHF orbitals. In this configuration, the orbital polarization functions ("single excitations") are expected to be larger than in type-1 cases.⁴ They are very important here because they compensate for the difference between the $1s^2 2s 2p^4 {}^4P$ RHF orbitals and those actually used to represent the $1s^2 2s 2p^4 {}^4P$ configuration. This compensation effect is especially large in the $2p$ orbital where it is reflected in the $2p - \hat{f}'_p$ single excitations. In order to represent this compensation effect as well as possible, the \hat{f}'_p semi-internal orbital was represented with a $2p$ STO, instead of the $3p$ STO used in type-1 calculations.⁴ This compensation effect was found to be much smaller in $2s - \hat{f}'_s$ single excitations, and it is totally absent in \hat{f}'_d and \hat{f}'_f orbitals (because there are no d or f orbitals occupied in the $1s^2 2s 2p^4$ configuration). Therefore, the \hat{f}'_s , \hat{f}'_d , and \hat{f}'_f orbitals were represented with $3s$, $3d$, and $4f$ STO's, respectively, as was done in type-1 cases.⁴

The four exponential factors α_{3s} , α_{2p} , α_{3d} , and α_{4f} were determined by minimizing the energy of the trial wave function (i.e., second-lowest eigenvalue) with respect to independent variations of each of their values. The resulting NCMET charge wave function, ${}^4P(1)$, is shown in the second column of Table II. This wave function is a true variational bound (energy-wise) to the second exact wave function of 4P symmetry because there is another eigenvector of the same CI matrix with lower energy. This lower eigenvector ${}^4P(0)$ is given in the third column of Table II for comparison. Both of those wave functions, ${}^4P(0)$ and ${}^4P(1)$, have large contributions from both $2s 2p^4$ and $2s^2 2p^2 3s$ configurations. The configurational assignments, however, are unambiguously ${}^4P(0) \cong 2s^2 2p^2 3s$ and ${}^4P(1) \cong 2s 2p^4$, in agreement with experimental assignments.¹⁷

The results of two previous calculations on the $2s 2p^4$ configuration are given in the fourth and fifth columns of Table II. Both of these previous calculations used $1s$, $2s$, and $2p$ radial functions taken from the $2s 2p^4 {}^4P$ RHF wave function, and

both calculations failed to include an adequate representation of the $2s^2 2p^2 3s$ configuration. As a result, there is no lower-lying state of 4P symmetry in either case and both must be considered approximations to the ${}^4P(0)$ state. In both of the previous calculations, the coefficients of the $2s 2p^4$, $2p^2 \hat{f}'_d$, $2p^3 \hat{f}'_f$, and $2p^4 \hat{f}'_d$ configurations are very close to the corresponding values in the ${}^4P(1)$ wave function of this work (where \hat{f}'_d is substituted for \hat{f}_d), except²¹ for the $2p^3 \hat{f}'_f$ of Ref. 2. In the calculation of Ref. 4, however, the important $2s 2p^2 3s$ configuration is essentially missing entirely, and the $2s^2 2p^2 \hat{f}'_s$ coefficient approximates that of the $2s^2 2p^2 \hat{f}'_s$ of the ${}^4P(0)$ of this work. In the wave function of Ref. 8(b) (fifth column), an attempt to improve on the results of Ref. 4, the \hat{f}'_s exponential factor α_{3s} has become much smaller, making the \hat{f}'_s orbital more diffuse and $3s$ like, and the magnitude of the $2s^2 2p^2 \hat{f}'_s$ coefficient has increased markedly over that of Ref. 4. The sign of this coefficient, however, indicates that it is approaching the $2s^2 2p^2 3s$ coefficient of the ${}^4P(0)$ state and not the ${}^4P(1)$. Both of these previously calculated wave functions, therefore, may be said to have a sort of dual character, resembling, in part, the ${}^4P(0)$ state and, in part, the ${}^4P(1)$ state. The result is poor approximations to both, as indicated in Table III, which shows that the ${}^4P(1)$ eigenvalue (i.e., the *second*-lowest eigenvalue) of this work is lower than the lowest eigenvalues ${}^4P(0)$ obtained in either of the previous calculations.

Another important difference between the results of this work and the previous calculations is the large size of the $2s 2p^3 \hat{f}'_p(1)$ coefficient in the ${}^4P(1)$ wave function of this work. This is caused by the compensation effect of $2p - \hat{f}'_p$ single excitations, which correct the $2s 2p^4$ configuration for the difference between the $2p$ orbital of the $2s 2p^4 {}^4P$ RHF wave function and the $2p$ orbital (determined by the $2s^2 2p^2 3s {}^4P$ RHF wave function) used in this work. The result is effectively equivalent to the use of two different (nonorthogonal) $2p$ orbitals in the same wave function without the computational complications which arise from the use of nonorthogonal orbitals.

The oxygen atom $2s 2p^5 {}^3P^o$: This state is very similar to the nitrogen atom $2s 2p^4 {}^4P$, except that in this case a " $3d$ state," i.e., the $2s^2 2p^3 ({}^2D^o) 3d {}^3P^o$ state, also lies below the $2s 2p^5 {}^3P^o$, as well as the " $3s$ state," $2s^2 2p^3 ({}^2P^o) 3s {}^3P^o$. Consequently the $2s 2p^5$ configuration corresponds to the third state of ${}^3P^o$ symmetry, and the $\hat{f}'_d = \hat{f}'_d + 3d$ division, which was optional in the nitrogen $2s 2p^4 {}^4P$, is variationally required in this case. This state also happens to lie above the $2s^2 2p^3 {}^4S^o$ state of the oxygen +1 ion and therefore falls in the corre-

TABLE III. Comparison of nondynamical correlation energies $\Delta E(\text{nondyn}) = E(\Psi_c) - E_{\text{RHF}}$ of this work and energies of previous calculations for $2s2p^n$ states not lowest of their symmetry. In this work, the number of lower roots (matrix eigenvalues and eigenvectors) of the same symmetry is equal to the number indicated by experimental assignments in every case. The other results are not variational bounds on the energies of the states indicated here.

Electronic state	No. of lower states ^a	$\Delta E = E(\Psi) - E(\text{RHF})$			$E(\text{RHF})$
		This work (Luken and Sinanoğlu)	Öksüz ^b	Nicolaides ^c	
Carbon $2s2p^3\ ^3P^o$	1	-1.562	•••	-1.126	-1015.945
Nitrogen +1 $2s2p^3\ ^1P^o$	1	-1.170	-1.344	-1.747	-1444.869
Nitrogen $2s2p^4\ ^4P$	1	-1.615	-0.978	-1.351	-1469.004
Oxygen +1 $2s2p^4\ ^2P$	1	-3.204	-2.523	-3.402	-1994.781
Oxygen $2s2p^5\ ^3P^o$	2	-2.565	-1.947	-2.695	-2018.520
Fluorine +1 $2s2p^5\ ^1P^o$	1	-3.333	-2.962	-3.081	-2657.106

^a Reference 17.

^b Reference 4 (Paper I). In this work the variational parameters were restricted to prevent variational collapse.

^c See Ref. 8(b) (cf. footnote d of Table II).

sponding continuum. Interaction with this continuum (e.g., autoionization), however, is symmetry forbidden in L - S coupling and (nonrelativistically at least) this continuum can be rigorously ignored.

The NCMET charge wave function was calculated in the same manner as in the nitrogen case, except that in this case the third-lowest $^3P^o$ eigenvalue of the CI matrix was minimized as required here instead of the second required in that case. In particular, the $1s$, $2s$, $2p$, and $3s$ radial functions were taken from the $2s^22p^3(^2P^o)3s\ ^3P^o$ RHF wave function—the lowest one of $^3P^o$ symmetry—and a hydrogenic radial function $r^2 \exp(-\frac{1}{3}r)$ was used for the $3d$ orbital. Likewise, the \hat{f}'_s , \hat{f}'_p , \hat{f}'_d , and \hat{f}'_f semi-internal orbitals were represented with $3s$, $2p$, $3d$, and $4f$ STO's, respectively, Schmidt-orthogonalized to the $1s$, $2s$, $2p$, $3s$, and $3d$ orbitals.

The energies of the three lowest $^3P^o$ eigenvalues obtained in this case are plotted in Fig. 2, along with their RHF and experimental energies. The procedure used to generate exact L^2 , S^2 eigenstates in this calculation also produces eigenvectors for all additional symmetries with $L \geq 1$ and $S \geq 1$ which can be formed by any configuration in the basis set.²² The energies of these additional eigenvectors of other symmetries which fall below the third $^3P^o$ eigenvector are also plotted in Fig. 2 for comparison. The left side of Fig. 2 indicates the RHF energies for the $2s2p^5\ ^3P^o$ configuration and all $2p^33s$ and $2p^33d$ states with $L \geq 1$ and $S \geq 1$. Note that in this (RHF/orbital) approximation, the $2p^3(^2P^o)3d$ and $2s2p^5\ ^3P^o$ configurations are reversed from the correct order, and, among these configurations, the $2s2p^5$ is the fourth one of $^3P^o$ symmetry.

The RHF energies in Fig. 2 are plotted relative

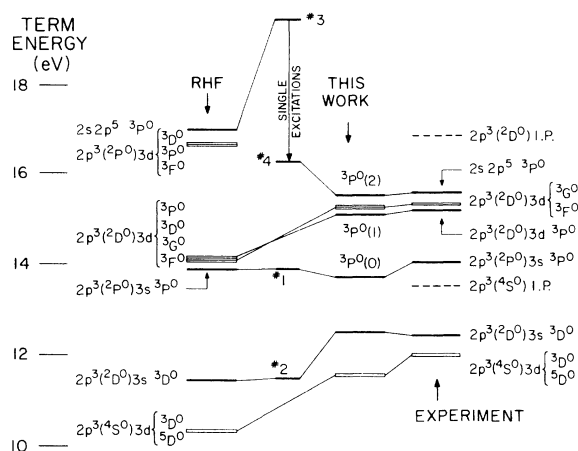


FIG. 2. Theoretical and experimental term energies in the oxygen atom. The energies labeled "this work" are the lowest nine eigenvalues of the CI matrix used to calculate the $2s2p^5\ ^3P^o$ NCMET charge wave function. These are plotted relative to the energy of the $2s2p^4\ ^3P$ charge wave function (Ref. 2). These are compared to the corresponding restricted Hartree-Fock (RHF) energies (Refs. 20 and 23) on the left, plotted relative to the energy of the $2s^22p^4\ ^3P$ RHF wave function, and to the experimental term energies (Ref. 17) on the right. The levels labeled No. 1, No. 2, No. 3, and No. 4 are explained in the text. The levels labeled $^3P^o(0)$, $^3P^o(1)$, and $^3P^o(2)$ are the first, second, and third $^3P^o$ eigenvalues, respectively. Groups of levels which are too close together to plot separately are connected with vertical lines. The purpose here is merely to show the level orderings as obtained at this point in the calculations of these states. The total energies of these states as indicated by NCMET also include additional all-external correlation energies (ΔE_{ext}) (see Refs. 1 and 4) which have not been entered into the energies plotted here.

to the RHF energy of the $2s^2 2p^4 {}^3P$ ground state. These energies represent separate SCF (self-consistent field) calculations on each state,^{20,23} resulting in different $1s$, $2s$, $2p$, $3s$, and $3d$ orbitals in each case. For practical reasons, it is necessary to use a single set of these orbitals in a CI calculation on these configurations. Except for the $2s 2p^5$, however, there is very little difference between the $1s$, $2s$, $2p$, and $3s$ or $3d$ orbitals in one of these states and those in any other. In this case, the $1s$, $2s$, $2p$, and $3s$ orbitals from the $2p^3({}^2P^o)3s {}^3P^o$ RHF wave function—the lowest ${}^3P^o$ —and a hydrogenic $3d$ were used in every configuration. The energy of the $2p^3({}^2P^o)3s {}^3P^o$ itself, indicated by level No. 1 in Fig. 2, is unchanged by this choice of orbitals. The energy of the $2p^3({}^2D^o)3s {}^3D^o$, for example, is slightly elevated over its RHF energy by using these orbitals instead of its own RHF orbitals. As shown by level No. 2 in Fig. 2, however, this change, amounting to only about 0.02 eV, is practically imperceptible. The energies of the $2p^3 3d$ states are also slightly raised by this choice of orbitals, but, as with the $2p^3({}^2D^o)3s {}^3D^o$, the change is extremely small.

In contrast to the $2p^3 3s$ and $2p^3 3d$ states, the energy of the $2s 2p^5 {}^3P^o$ as indicated by level No. 3 in Fig. 2, rises more than 2 eV over its RHF energy when using $1s$, $2s$, and $2p$ orbitals taken from the $2p^3({}^2P^o)3s {}^3P^o$ RHF wave function instead of its own RHF orbitals. This elevation, however, is more than overcome by the compensation effects of single excitations, especially the $2p - \hat{f}_p$ excitations (i.e., $2s 2p^5 - 2s 2p^4 \hat{f}_p$), which effectively drop the $2s 2p^5 {}^3P^o$ configuration from level No. 3 to level No. 4 in Fig. 2. Level No. 4 is actually below the RHF energy of the $2s 2p^5 {}^3P^o$ because the single configuration + single excitations energy represents a slightly more flexible wave function than the strictly single configurational RHF wave function.

The energies labeled “this work” in Fig. 2 are the nine lowest eigenvalues of the CI matrix used to calculate the $2s 2p^5 {}^3P^o$ charge wave function (plotted relative to the energy of the $2s^2 2p^4 {}^3P$ charge wave function). This matrix includes all of the configurations on the left side of Fig. 2 plus all additional configurations (including single excitations, etc.) required by NCMET^{1,4} to complete the $2s 2p^5 {}^3P^o$ charge wave function. These eigenvalues correspond to the semi-internal orbital exponential factors (α_{3s} , α_{2p} , α_{3d} , and α_{4f}) which minimize the third ${}^3P^o$ eigenvalue, labeled ${}^3P^o(2)$ in Fig. 2. The lower-two ${}^3P^o$ eigenvalues ${}^3P^o(0)$ and ${}^3P^o(1)$ and the other six eigenvalues indicated in Fig. 2, all came automatically out of the same matrix. Other than minimizing the ${}^3P^o(2)$

energy, nothing at all was done to specifically improve any of these lower eigenvalues. The corresponding experimental term energies¹⁷ are given on the right side of Fig. 2. In every case, theoretical configuration and symmetry assignments, based on configurational vector coefficients, are in complete agreement with the correspondingly ordered experimental assignments, except for the $2p^3({}^2D^o)3d {}^3D^o$ which is absent from the experimental (optical) observations¹⁷ because of rapid autoionization into the ${}^4S^o$ continuum.

In addition to correct ordering, the separation of the eigenvalues obtained in this work are in remarkably good agreement with experiment.²⁴ The relative separations of the RHF energies, in contrast, are not even qualitatively correct. For example, the $2s 2p^5 {}^3P^o - 2p^3({}^2D^o)3d {}^3P^o / 2p^3({}^2D^o)3d {}^3P^o - 2p^3({}^2P^o)3s {}^3P^o$ term splitting ratio has the value 13.9 for RHF energies, 0.29 in this work, and 0.30 in experiment.^{17,24}

Nitrogen + 1 ion $2s 2p^3 {}^1P^o$, oxygen + 1 ion $2s 2p^4 {}^2P$, and fluorine + 1 ion $2s 2p^5 {}^1P^o$. Like the nitrogen atom $2s 2p^4 {}^4P$, these three cases each have a single lower-lying “ $3s$ state,” i.e., the $2s^2 2p^3 3s {}^1P^o$, $2s^2 2p^2 3s {}^2P$, and $2s^2 2p^3 3s {}^1P^o$, respectively. The NCMET charge wave functions for these cases were calculated with the same method used for the nitrogen $2s 2p^4 {}^4P$. In particular, the $1s$, $2s$, $2p$, and $3s$ orbitals used in these cases were taken from the $2s^2 2p^3 3s {}^1P^o$ and $2s^2 2p^2 3s {}^2P$ RHF wave functions, respectively. For the $3d$ orbitals, a hydrogenic radial function of the form $r^2 \exp(-2r/3)$ with an effective nuclear charge of +2 was used because the $3d$ electron will now see net charges of +2 in each of these cases. The semi-internal exponential factors α_{3s} , α_{2p} , α_{3d} , and α_{4f} were determined by minimizing the second-lowest ${}^1P^o$ eigenvalue in the nitrogen ion, the second-lowest 2P eigenvalue in the oxygen ion, and the second-lowest ${}^1P^o$ eigenvalue in the fluorine ion. The resulting minimum energies are indicated in Table III. In all three ions, the configurational assignments indicated by the configurational coefficients in the two-lowest ${}^1P^o$, 2P , and ${}^1P^o$ eigenvectors, respectively, agree with the correspondingly ordered experimental assignments.¹⁷

As indicated in Table III, the final energies obtained in this work are higher than those obtained in Ref. 8(b). The results of Ref. 8(b), however, represent the lowest eigenvalues, instead of the second-lowest eigenvalues, thus the wrong state has been minimized in Ref. 8(b). For these cases, therefore, the results of Ref. 8(b) are not variationally bounded by the states of interest (i.e., $2s 2p^3 {}^1P^o$ and $2s 2p^4 {}^2P$), and the fact that the energies of Ref. 8(b) for the nitrogen and oxygen ions

are lower than those obtained here does not imply that the results of Ref. 8(b) are more accurate than the results of this work. On the contrary, the lowness of the Ref. 8(b) energies demonstrates that the Ref. 8(b) wave functions are variationally collapsing to the lower-lying $2s^2 2p 3s^1 P^o$ and $2s^2 2p^2 3s^2 P$ states, i.e., to the wrong states.

Carbon atom $2s 2p^3 P^o$: This case is again very much like the nitrogen atom $2s 2p^4 P$ state discussed above. The $1s$, $2s$, $2p$, and $3s$ radial functions were taken from the $1s^2 2s^2 2p 3s^3 P^o$ RHF wave function and $r^2 \exp(-r/3)$ was used for the $3d$ radial function. In this case, the lower-lying $2s^2 2p 3s^3 P^o$ falls well below the $2s 2p^3 P^o$ configuration and causes no special difficulties. The $2s^2 2p 3d^3 P^o$ configuration, however, lies extremely close to the $2s 2p^3 P^o$, resulting in an extreme near degeneracy. In addition, the $2s^2 2p 4s^3 P^o$ lies in between the $2s 2p^3 P^o$ and $2s^2 2p 3d^3 P^o$ states, although it interacts very weakly with both of these states because of the extremely diffuse nature of the $4s$ orbital. The result is that the four lowest $3P^o$ eigenvectors obtained in this work clearly indicate (on the basis of their configurational vector coefficients) that the lowest and third-lowest $3P^o$ states should be assigned to the $2s^2 2p^2 3s$ and $2s^2 2p^2 4s$ configurations, respectively. The second- and fourth-lowest eigenvectors, however, both contain nearly equal amounts of $2s 2p^3$ and $2s^2 2p 3d$ configurations. In this calculation, the semi-internal exponential factors were chosen to minimize the second $3P^o$ eigenvalue, in accordance with the experimental assignment of the $2s 2p^3$ configuration to the second state of $3P^o$ symmetry in carbon.¹⁷ This assignment is purely conventional however, and this state would be better labeled as simply the "second $3P^o$ state" of the carbon atom.

Boron $2s 2p^2 S$: This state is very different from the other $2s 2p^n$ upper states. In this case there are no lower or nearby $2S$ configurations containing a $3d$ orbital. There are, however, four lower states of the form $2s^2 n s^2 S$, with $N = 3, 4, 5$, and 6 . These are all included in the $2s^2 \hat{f}_s$ semi-internal configuration. In order to represent each of these lower states, it is necessary to separate the f_s semi-internal orbital into five orthogonal parts,

$$\hat{f}_s(\vec{r}) = 3s(\vec{r}) + 4s(\vec{r}) + 5s(\vec{r}) + 6s(\vec{r}) + \hat{f}'_s(\vec{r}),$$

each of which is also orthogonal to the $1s$ and $2s$ orbitals of this state. The charge wave function of this state was not calculated in the current work because of the unusual computational requirements unique to this state. In principle, however, this state would be treated in the same manner as the states discussed above. In this

case, the radial parts of the $1s$, $2s$, and $3s$ orbitals would be taken from the $1s^2 2s^2 3s^2 S$ RHF wave function. The $2p$ radial function would be taken from the $1s^2 2s 2p^2 S$ RHF wave function. The $4s$, $5s$, and $6s$ radial functions could be taken either as hydrogenic radial functions (perhaps with a quantum defect to be determined variationally) or from $1s^2 2s^2 4s$, $5s$, and $6s^2 S$ RHF wave functions.²⁵ The \hat{f}_s , \hat{f}_p , and \hat{f}_d semi-internal orbitals (no f -symmetry orbitals are present in this case) would then be determined variationally by minimizing the fifth-lowest root of $2S$ symmetry of the resulting Hamiltonian matrix.

V. OPTICAL OSCILLATOR STRENGTHS INVOLVING STATES NOT LOWEST OF THEIR SYMMETRY

To test the wave functions described above we calculated the optical oscillator strengths of several transitions involving excited states not lowest of their symmetry. Oscillator strengths are known to be very sensitive to non-closed-shell electron correlation effects,^{5,26} all of which are specified by NCMET and included in the NCMET charge wave function^{1,4,7} as found by Sinanoğlu. Among L -shell transitions, i.e., $2s^2 2p^n \rightarrow 2s 2p^{n+2}$, between type-1 states, for example, f values calculated with NCMET charge wave functions for both upper and lower states generally agreed with accurate experimental f values to within about 10%,^{5,26,27} confirming the Sinanoğlu theory very well, whereas the f values calculated using RHF and other previous available theories turned out to be often in error by factors as large as 2–3 (for these same L -shell transitions; larger errors with some in M shells).

The theory of L - S coupled multiplet oscillator strengths has been given previously⁵ and will not be repeated here. Multiplet absorption f values we calculated using both the "length" (f_r) and "velocity" (f_v) formulas are reported in Table IV for seven transitions with type-3 upper states. The RHF, NCMET, and most other f values in Table IV were calculated using highly accurate experimental energies in the formulas for f_f and f_v . Completely nonempirical f values can be obtained, if desired, by using the (geometric) mean $f_m = (f_r f_v)^{1/2}$ which is independent of this energy factor.^{5,26}

The RHF f values reported in Table IV were calculated using single configurational RHF wave functions for both upper and lower states obtained from separate SCF calculations on each state. We used previously published RHF wave functions^{23,28} in most cases, some we calculated ourselves. The resulting nonorthogonality of upper- and lower-state orbitals was fully treated as described

TABLE IV. Multiplet absorption oscillator strengths for transitions involving upper states which are not the lowest of their symmetry. Theoretical f values are given in both "length" (upper entry) and "velocity" (lower entry) forms, where available, using experimental wavelengths λ . The values of λ are given below in angstroms. Experimental f values are reported for beam-foil, phase-shift, and arc intensity measurements. The less accurate arc measurements are enclosed in parenthesis.

Transition and wavelength (λ)	RHF	Theoretical f values			NCMET ^c (this work)	Experiment f^{E1} values
		Westhaus and Sinanoğlu ^a	Nicolaides ^b	Other		
C I $2p^2\ ^3P \rightarrow 2p^3\ ^3P^o$ (1329)	0.169	...	0.092	0.097 ^d	0.038	(0.039) ^e
	0.115	0.105 ^d	0.059	
N II $2p^2\ ^1D \rightarrow 2p^3\ ^1P^o$ (660)	0.240	0.286	0.324	...	0.157	0.13 ^{f,g}
	0.096	0.272	0.160	0.12 ^{f,h}
N II $2p^2\ ^1S \rightarrow 2p^3\ ^1P^o$ (746)	0.847	0.255	0.195	...	0.255	0.25 ^{f,g}
	0.441	0.314	0.340	0.22 ^{f,h}
Ni $2p^3\ ^4S^o \rightarrow 2p^4\ ^4P$ (1134)						0.058 ⁱ
	0.490	0.181	0.286	...	0.035	0.078 ^j
	0.557	0.141	0.077	0.080 ^k
O II $2p^3\ ^2D^o \rightarrow 2p^4\ ^2P$ (538)						0.083 ^l
						(0.13) ^m
	0.329	...	0.311	...	0.158	0.166 ^{f,n}
	0.143	0.184	0.153 ^{f,o}
O II $2p^3\ ^2P^o \rightarrow 2p^4\ ^2P$ (581)						0.142 ^{f,p}
	0.304	...	0.007	...	0.086	0.099 ^{f,n}
	0.155	0.120	0.091 ^{f,o}
O I $2p^4\ ^3P\ 2p^5\ ^3P^o$ (792)	0.344	...	0.190		0.088	(autoionizes) ^q
	0.328		0.147	

^a See Ref. 5. Most neutral and +1 ion calculations involving "nonlowest states" were deliberately not carried out by Westhaus and Sinanoğlu pending a proper variational approach for such special cases. A couple or so cases given used the Öksüz-Sinanoğlu nonvaried wave functions. All other Westhaus-Sinanoğlu results were with type-1 states and therefore expected to be accurate at the time, as they have turned out.

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previously.⁵

Likewise, the NCMET f values in Table IV we calculated using NCMET charge wave functions for both upper and lower states. The upper states are each of type 3, and each was represented with the NCMET charge wave function of the state described in Sec. IV. The lower state in each of these transitions is of type 1. We calculated the

NCMET charge wave function for these states as previously described^{1,4} by Sinanoğlu and Öksüz with the minor refinements mentioned earlier in this paper.

The f values of Refs. 5 and 8(a) which are included in Table IV were calculated also with the Sinanoğlu NCMET using lower-state wave functions nearly identical to those used in this work (however, the

wave functions for the upper states differing as described above). Previous calculations⁵ have demonstrated that these NCMET charge wave functions accurately represent each of the type-1 states involved. The accuracy of the f values in each of these calculations [Refs. 5 and 8(a), and this work], therefore, is expected to depend primarily on the accuracy of the upper-state (type 3) wave functions used in each case. Where experimental f values have been available, previous calculations involving nonlowest-type states have all been previously noted for their large discrepancies.^{4, 8(a)} As can be seen in Table IV, the NCMET results of this work, which use the variationally appropriate upper-state charge wave functions for the first time, are in much better agreement with experiment in every case.²⁹

The NCMET f values obtained in this work, although much better than any previous calculations on these nonlowest-state-type transitions, are not as accurate (i.e., 10%) as most NCMET f values previously calculated for type-1 \rightarrow type-1 transitions.⁵ One reason for this is the larger magnitude of the semi-internal and internal mixing effects found in the type-3 states considered here. This would make some additional effects such as the "unlinked products" of semi-internal orbitals which Sinanoğlu has recently discussed³⁰ and called "quasi-all-external correlations," more significant in these neutral and +1 ions as compared to the previous higher positive ions.⁵ Such additional effects are easily included in NCMET, but these refinements will not be attempted here, the present results already constituting a major improvement over any theoretical values available before.^{8(b)}

In the NII and OII transitions, comparison of theory with experiment is complicated by the requirement of a branching ratio for converting experimental (lifetime) data into f values. The "experimental" f values for these transitions given in Table IV were calculated using the NCMET branching ratios obtained in this work. This may seem to favor comparison with the theoretical f values of this work; however, similar experimental f values were calculated using all possible branching ratios obtainable from previous calculations, as well as those of this work, and in no other case was the agreement between theory and experiment as good as it is for the NCMET values given in Table IV. Further details on each of these cases will be published later.³¹

In addition to the optical oscillator strengths reported here, the type-3 wave functions obtained in this work have also been used by Davis and Sinanoğlu to calculate generalized oscillator strengths and electron scattering cross sections

in the Born approximation. Details and results of these calculations are reported elsewhere.¹⁰

VI. CONCLUSIONS

We classified the ground and excited electronic states of atoms and molecules into four categories based on their configuration labels and those of lower-lying states: Type-1 states are lowest of their symmetry; type-2 states have a finite number of lower states of the same symmetry, whose ordering is determined by their configuration labels; type-3 states include all other states with a finite number of lower states of the same symmetry; and type-4 states lie above an infinite number of lower states of the same symmetry.

In Sec. II, variational methods for calculating wave functions were outlined for each of the categories.

Type-2 and type-3 states can be properly treated using the Hylleraas-Undheim-MacDonald (HUM) theorem.¹²⁻¹⁴ In this approach, energy-wise variationally bounded trial wave functions are calculated by selecting specific eigenvectors of matrix representations of the electronic Hamiltonian. In particular, if the state of interest is the n th state of symmetry γ , then it is necessary to always select and stick to the n th-lowest γ symmetry eigenvector of the Hamiltonian matrix during all variations.

In atoms and molecules it is usually convenient to use a set of single configurational N -electron wave functions as a basis for determining the Hamiltonian matrix. This set must include the configuration of the state of interest, as well as explicit (i.e., linearly independent) representations of all lower-lying configurations. The configuration labels of these basis functions, however, cannot be used as a means of selecting variational eigenvectors. This selection is determined strictly by the number of states of the same symmetry below the state of interest. If the expected configurational assignment is correct, it will automatically be reflected in the specified eigenvector for a properly chosen basis set. Selection of a lower eigenvector in order to force a configuration label (that is, choosing a particular root because it has a large coefficient on the configuration of interest) will cause a partial variational collapse to a lower state, resulting in poor approximations to both the lower state and the state of interest.

Construction of an adequate basis set is especially easy for type-2 states because the order and separations of the variationally required configurations are characteristically insensitive to the choice of the orbitals found in these configurations. In general, any reasonable choice of orbitals will

give qualitatively correct results, and, except for selection of a nonlowest eigenvalue, the variational treatment of these states is almost identical to the treatment of type-1 states.

For type-3 states, however, the order and separations of the variationally required configurations are often very sensitive to small changes in the orbitals. In the nitrogen atom, for example, it was demonstrated that the differences between the RHF orbitals of two adjacent configurations are sufficient to drastically change the relative energies of these configurations. In such cases, the practical rule, "minimize lowest states first," can prevent accidental degeneracies and reversals which can be caused by representing the configuration of the state of interest better than lower-lying configurations.

Methods^{18,19} exist for treating type-4 states, but these do not include the HUM method. Attempts to apply the HUM method to such states, without further constraints, can lead to serious errors, as in the $2p^2\ ^1S$ BeI case.^{8,9}

In Sec. III of this paper, NCMET charge wave functions were calculated for six particular type-3 states with $2s2p^n$ configurations. In each case, difficulties in constructing adequate basis sets have led to erroneous results in previous attempts⁸ to calculate variational wave functions for these states. In the current work, based on the HUM theorem, the variational difficulties involved were overcome by observing the following rules:

First, each lower configuration must be explicitly represented in the variational basis set. In these cases, this required certain semi-internal orbitals to be split into two or more parts in order to represent the lower states and remaining semi-internal effects separately.

Secondly, the lowest states should be (roughly) minimized first, prior to careful minimization of the state of interest. In the current work, this meant taking the $1s$, $2s$, $2p$, and $3s$ orbitals from the RHF wave function of the lowest configuration with the symmetry of interest, and not from the RHF wave function of the configuration of interest itself.

Thirdly, configuration labels must be ignored during the variational process. In this work this meant sticking to a specific eigenvalue, e.g., the second or third of a particular symmetry, and assigning configuration labels only after this eigenvalue has been minimized, and only according to the magnitudes of the coefficient in the wave function (configuration label means one configuration has noticeably larger coefficients than any of the others in the eigenvector).

In these calculations, variationally correct wave functions were obtained for each of these states

for the first time, which indicate that previous attempts⁸ have been in error. In each case except one, the configurational assignments found in this work are in complete agreement with the correspondingly ordered experimental assignments for the state of interest and all lower states. The one exception is the carbon $2s2p^3\ ^3P^o$, where configuration mixing with the $2s^22p3d\ ^3P^o$ is too heavy to permit meaningful assignments. In each case, the theoretical configuration assignments found in this work came out automatically and naturally without any preconceived attention to configuration labels beyond the three rules outlined above.

Examination of the wave functions obtained has revealed that, unlike the situation in type-1 states, single excitations ("orbital polarizations") from the configuration of interest, especially $2p \rightarrow \hat{f}_p$ excitations, are very important in these states. These single excitations effectively compensate for the difference between the Hartree-Fock radial functions of the state of interest and those used here, which were determined by another lower-lying configuration.

As a final test of these wave functions, they were used to calculate oscillator strengths for several transitions involving states not lowest of their symmetry. In each case where experimental data has been available, many of the discrepancies,^{5,8,20,32} which existed with previous calculations on these transitions, have now been resolved with the f values obtained here.

Among L -shell states, the set of all type-3 states collectively constitute a very small and exceptional subset. Among larger atoms and molecules, however, this type of state will occur with rapidly increasing frequency. In M -shell configurations of atoms like magnesium, silicon, sulfur, etc., for example, similar situations involving $3s3p^m$ and $3s^23p^{m-2}3d$ configurations occur not only in neutral and singly ionized cases but also in highly ionized atoms like Fe^{+10} , etc. The situation is even worse in molecules where there are fewer symmetries and more states. Fewer states, therefore, can have the privilege of being the lowest of their symmetry. In addition, we note that the most difficult cases in atoms occur with the greatest frequency in neutral and singly ionized cases. Among stable free molecules, however, neutral and singly ionized cases are essentially all that exist.

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