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PHYSICAL REVIEW VOLUME 183, NUMBER 1 5 JULY 1969

Theory of Atomic Structure Including Electron Correlation. III. Calculations of Multiplet Oscillator Strengths and Comparisons with Experiments for C II, N I, N II, N III, O II, O III, O IV, F II, Ne II, and Na III

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(Received 20 February 1969)

The theory of atomic structure developed in the two preceding papers which treats electron correlation accurately in excited as well as ground states is applied to the evaluation of multiplet absorption oscillator strengths for a number of transitions of the type of $1s^22s^22p^n \rightarrow 1s^22s2p^{n+1}$ in C II, N I, N II , N III, O II, O III, O IV, F II, Ne II, and Na III. Those types of correlation effects necessary to obtain accurate oscillator strengths are clearly indicated by the theory. The usual improvement on the Restricted Hartree-Fock (RHF) calculation, the mixing of those few configurations nearly degenerate with the RHF configuration, is by itself incapable of bringing the oscillator strengths into agreement with experimental values. All the nondynamical correlation effects given in the first paper of this series must be considered. Very detailed wave functions which contain those important nondynamical correlations were obtained in that paper and here are used to compute oscillator strengths. The results are compared extensively with recent experiments. The calculated values are usually in very good agreement with experimental data. Many more transitions for which no experimental results are yet available are also tabulated here.

I. INTRODUCTION

In the first two papers[1] of this series a theory which includes electron correlation effects in both the ground and excited states was developed and applied to several atomic properties. Methods for predicting and analyzing the N-electron correlation energies in states of nonclosed shell configurations were given and applied to 113 states of the $1s^22s^n2p^m (0 \leq n \leq 2, 0 \leq m \leq 6)$ configurations in atoms and ions with nuclear charge $5 \leq Z \leq 11$. Some of the excited configurations such as $1s^22s2p^3$ and $1s^22p^2$ contain inner holes. Theoretical electron affinities and excitation energies were obtained and compare favorably with experiment.

In this paper we present a way of applying this theory to predict allowed electric-dipole transition probabilities. Multiplet absorption oscillator strengths of 29 far-ultraviolet transitions of the type

$$1s^2 2s^2 2p^n (LS) \rightarrow 1s^2 2s 2p^{n+1} (L'S')$$

are calculated for the species C II, N I, N II, N III, O II, O III, O IV, F II, Ne II, and Na III. The wave functions obtained in I were used in these all-electron oscillator-strength calculations which are among the most detailed available to date. Recent lifetime measurements have been made for some of the transitions corresponding to the inverse emission process. Agreement between our results and experiment is very good.

A comparison is made among our results and previously calculated oscillator strengths, including those found in the National Bureau of Standards (NBS) Tables.[2] We find that although earlier calculations have included some of the specific configuration-interaction effects, the other nontransferable correlation effects obtained in I and II must be included to obtain the present good agreement with experiment. Where experimental data are not available, the remaining values predicted here are most credible and should be useful in astrophysics and atomic physics problems.

II. EXPRESSIONS FOR THE MULTIPLET OSCILLATOR STRENGTHS

The eigenfunctions of the nonrelativistic Hamiltonian for an N-electron system

$$H_{EL} = -\frac{\hbar^2}{2M} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \frac{Ze^2}{|\vec{r}_i|} + \sum_{1 \le i < j \le N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \tag{1}$$

can be labeled $\psi_{\gamma LSM_L M_S}$, with γ denoting the electronic configuration, L the total orbital angular momentum, S the total spin, and M_L and M_S their "Z" projections. The energy eigenvalues depend only on γ, L, and S. The multiplet oscillator strength is defined as[3,4]

$$f(\gamma LS \rightarrow \gamma' L'S') = \frac{2}{3} \frac{[E(\gamma' L'S') - E(\gamma LS)]}{(2L+1)(2S+1)} \mathcal{S}(\gamma LS \rightarrow \gamma' L'S'). \tag{2}$$

Atomic units ($\hbar = 1$, $m_e = 1$, $Q_e = 1$) are used throughout this paper; $f(\gamma LS \rightarrow \gamma' L'S')$ is dimensionless. $\mathcal{S}(\gamma LS \rightarrow \gamma' L'S')$ is the multiplet line strength and can be written in terms of the matrix elements of

$$\vec{R} = \sum_{i=1}^{N} \vec{r}_i \tag{3}$$

between degenerate states associated with the lower (γLS) and upper ($\gamma' L'S'$) terms:

$$\mathcal{S}(\gamma LS \rightarrow \gamma' L'S') = \sum_{M_L=-L}^{L} \sum_{M_S=-S}^{S} \times \sum_{M_{L'}=-L'}^{L'} \sum_{M_{S'}=-S'}^{S} \left| \frac{\int dx_1 \cdots dx_N \psi^*_{\gamma LSM_L M_S} \vec{R} \psi_{\gamma' L'S'M_{L'}M_{S'}}}{[(\psi_{\gamma LSM_L M_S} | \psi_{\gamma LSM_L M_S})(\psi_{\gamma' L'S'M_{L'}M_{S'}} | \psi_{\gamma' L'S'M_{L'}M_{S'}})]^{1/2}} \right|^2 . \tag{4}$$

Each nonvanishing term in the sum corresponds to a particular line in the multiplet spectrum which appears when a magnetic field is introduced. In (2) the factor $(2S+1)(2L+1)$ is the degeneracy of the initial (i.e., for absorption, the lower) term.

With the $\psi_{\gamma LSM_L M_S}$ as eigenfunctions of H_{EL}, the commutation relations of H_{EL} with $\vec{R}$ lead to two additional expressions[5,6] for $\mathcal{S}(\gamma LS \rightarrow \gamma' L'S')$:

$$\mathcal{S}(\gamma LS \rightarrow \gamma' L'S') = \frac{1}{[E(\gamma' L'S') - E(\gamma LS)]^2} \sum_{M_L} \sum_{M_S} \sum_{M_{L'}} \sum_{M_{S'}} \left| \frac{(\psi_{\gamma LSM_L M_S} | \vec{\nabla} | \psi_{\gamma' L'S'M_{L'}M_{S'}})}{\{\|\psi_{\gamma LSM_L M_S}\| \cdot \|\psi_{\gamma' L'S'M_{L'}M_{S'}}\|\}} \right|^2 \tag{5}$$

and

$$\mathcal{S}(\gamma LS \rightarrow \gamma' L'S') = \frac{1}{[E(\gamma' L'S') - E(\gamma LS)]^4} \sum_{M_L} \sum_{M_S} \sum_{M_{L'}} \sum_{M_{S'}} \left| \frac{(\psi_{\gamma LSM_L M_S} | \vec{A} | \psi_{\gamma' L'S'M_{L'}M_{S'}})}{\{\|\psi_{\gamma LSM_L M_S}\| \cdot \|\psi_{\gamma' L'S'M_{L'}M_{S'}}\|\}} \right|^2 . \tag{6}$$

Here we have defined the sums of one-electron operators

$$\vec{\nabla} = \sum_{i=1}^{N} \vec{\nabla}_i \tag{7}$$

and
$$\vec{A} = \sum_{i=1}^{N} \frac{Ze^2\vec{r}_i}{|\vec{r}_i|^3} . \tag{8}$$

We shall use the notation $\mathcal{S}_R$, $\mathcal{S}_\nabla$, $\mathcal{S}_A$ to denote the multiplet line strengths computed via formulas (4), (5), and (6), respectively, with corresponding symbols for the oscillator strengths derived from them. We shall call $\vec{R}$, $\vec{\nabla}$, and $\vec{A}$ the dipole-length, dipole-velocity, and dipole-acceleration operators.

If, as is usually the case, expressions (4), (5), and (6) are evaluated with only approximate eigenfunctions, the numerical results of the three calculations no longer necessarily agree. However, none of these formulas is theoretically more fundamental than the other two; each, in fact, has a classical analog.[6] Thus *a priori* we should consider the results obtained with $\mathcal{S}_R$, $\mathcal{S}_\nabla$, and $\mathcal{S}_A$ as having equal significance. In practical terms, however, when using only approximate wave functions we must allow ourselves the freedom to weight the results obtained with $\vec{R}$, $\vec{\nabla}$, and $\vec{A}$ according to the accuracy of these wave functions in the regions where they are most sensitive to the particular operator in question.

Since the acceleration operator contains terms behaving as $1/r^2$, $\mathcal{S}_A$ is most sensitive to the accuracy of the wave functions in the immediate neighborhood of the nucleus. On the other hand, both $\mathcal{S}_R$ and $\mathcal{S}_\nabla$ are sensitive to the wave functions in the atomic shell in which the reshuffling of electrons takes place. Actually, as Chandrasekhar[6] first pointed out for the ion H^-, the dipole-length operator emphasizes somewhat more distant regions than does the dipole-velocity operator, so that the oscillator strengths computed with variationally stable approximate wave functions are more trustworthily given in terms of the latter operator. This point of view seems to be generally appreciated for other atomic species, although as Weiss[7] points out by his example of the $2s^22p^2 \rightarrow 2s2p^3$ transition in C I, the very long range behavior of the atomic orbitals is unimportant in determining either $\mathcal{S}_R$ or $\mathcal{S}_\nabla$. Rather, in a more detailed consideration he finds the large contributions to both expressions coming from the region of the atomic shell where the charge density of the reshuffling electrons is large, with the dipole-velocity and dipole-length formulas, respectively, favoring the inner and outer portions of this shell. To calculate $\mathcal{S}_R$, $\mathcal{S}_\nabla$, and $\mathcal{S}_A$ with precision requires wave functions accurate over the entire configuration space of the electrons. Thus wave functions which are sensitive, for example, to the outer shell while neglecting a detailed description of configuration space near the nucleus might be expected to give $\mathcal{S}_R$ and $\mathcal{S}_\nabla$ accurately, but not $\mathcal{S}_A$.

In computing $f(\gamma LS \rightarrow \gamma' L' S')$ each term in the energy difference $E(\gamma' L' S') - E(\gamma LS)$ can be approximated by the expectation value of the Hamiltonian with respect to the corresponding approximate wave function. Alternatively, empirical values for this energy difference could be used, but then the calculation ceases to be a purely theoretical one. It is well known,[5] however, that the dependence of the numerical results upon this energy difference may be eliminated by taking the root mean square of f_R and f_∇ as the value for the oscillator strength. In cases in which there is no degeneracy associated with either term in the transition, this prescription also has other advantages.[8] We therefore will focus our attention on f_R and f_∇. To calculate the matrix elements of the one-electron operators in $\vec{R}$ and $\vec{\nabla}$ wave functions which accurately portray the charge distributions in the outer region associated with the reshuffling electrons are required for both the initial and final states. Classically, of course, it is the oscillating charge distribution which determines the radiation field.

When the transition can be described by a configuration change of a single particle outside a closed shell of $N-1$ passive particles, the usual independent-particle wave functions give rise to approximating the oscillator-strength formulas as one-body integrals between the initial and final orbital of the jumping electron.[4,9,10-11] When the Hartree-Fock (HF) procedure[10,11] is used to compute these initial and final orbitals, reliable results may be expected.[10] In fact, the semiempirical method of Bates and Damgaard,[9] the Coulomb Approximation, for obtaining the initial and final orbitals also leads to good results for f_R. However, when the transition involves the reshuffling of two or more equivalent electrons in open shells, the real charge densities are not usually portrayed to sufficient accuracy by the Restricted Hartree-Fock (RHF)[1,12] wave functions to give good oscillator strengths. There are exceptional cases, of course, but there is no reliable criterion for judging the accuracy of these calculations in general.[13] Indeed it has been pointed out by Weiss[10] and La Paglia[14] that agreement between f_R and f_∇ is certainly not a general criterion for accuracy of the results. In fact, we shall see in Sec. V that as a rule the RHF results for f_R and f_∇ do not even bound the actual value of the oscillator strength in open-shell systems. Clearly, the RHF wave functions must be supplemented by the inclusion of correlation effects in order to obtain reliable oscillator strengths. The problem is a formidable one if *all* types of correlation processes must be included. However, our intuitive notion that accurate oscillator strengths can be calculated with wave functions which simply represent the charge densities accurately suggests that only those correlation effects need be considered which have a direct bearing on the charge distribution. The nonclosed-shell many-electron theory of atoms and molecules (NCMET) developed in the preceding papers by Öksüz and Sinanoğlu speaks directly to this point by a detailed division and systematic analysis of the types of correlation processes which occur in atoms. Only certain types of correlations, well defined within the framework of NCMET, have a significant effect upon the charge distribution.

III. NONCLOSED-SHELL MANY-ELECTRON THEORY OF ATOMS AND MOLECULES AND THE CALCULATION OF OSCILLATOR STRENGTHS

To review briefly the electronic correlation problem treated in I, we recall that for closed-shell states[15-18] the main correlation effects are between all possible pairs of electrons occupying spin orbitals, say, i and j, in the filled HF sea. More generally any number of the N particles may correlate with each other and so the exact wave function can be written[17]

$$\psi=\mathcal{A}(N)\left[(1\,2\cdots N)\cdot\left(1+\sum_{i=1}^{N}\frac{\hat{f}_i}{(i)}+\sum_{i<j}^{N}\frac{1}{2^{1/2}}\frac{\hat{U}'_{ij}}{(ij)}+\sum_{i<j<k}\frac{1}{(3\,!)^{1/2}}\frac{\hat{U}'_{ijk}}{(ijk)}+\cdots\right)\right]. \tag{9}$$

Here, the single determinant $\mathcal{A}(N)$ $(1\,2\cdots N)$ represents the HF orbital wave function and the $\hat{f}_i$, $\hat{U}'_{ij}$, $\cdots$, $\hat{U}'_{i_1 i_2\cdots i_n}$, $\cdots$ are the 1, 2, ... n, ...-electron correlation functions, whose properties are discussed in earlier references.[17, 18] $\alpha(n)$ is the n-electron antisymmetrizer. Owing to the properties of the HF orbitals, the short range of the residual "fluctuation potential," and the exclusion principle, correlations involving an odd number (1, 3, 5, ...) of particles are small while correlations among an even number of particles can be approximated as the sum of unlinked products[17, 18]:

$$\hat{U}'_{ijkl}\approx\hat{U}_{ijkl}=\tfrac{1}{2}\mathcal{A}(4)(\hat{U}'_{ij}\hat{U}'_{kl}+\hat{U}'_{ik}\hat{U}'_{jl}+\hat{U}'_{il}\hat{U}'_{jk}). \tag{10}$$

The dominant corrections to the HF wave function are the two-particle functions out of the HF sea and it is found that the corresponding corrections to the HF charge density (the expectation value of a one-electron operator) are small.[17, 18] That is, for closed-shell states the atomic charge distribution is already quite accurately given by the HF calculation. The closed-shell many-electron theory (MET)[17, 18] is also readily applicable to the case in which a single electron is found outside a completed shell.

The perturbation-theory treatment of general nonclosed shell states by Silverstone and Sinanoğlu[19] led to their discovery of some types of correlation effects unique to open shells. These arise because the HF sea $\varphi_1\varphi_2\cdots\varphi_M$ is not completely filled as in the closed-shell case, i.e., $M>N$. In terms of an independent-particle model based on the RHF wave function Φ_{RHF}, there are two nonclosed-shell–type correlation effects: the "internal" and "semi-internal" correlations.[1] The former consist, for example, of two particles being virtually excited from the orbitals they originally occupied in Φ_{RHF} to previously vacant orbitals within the HF sea. The latter involve, for example, two-particle correlations in which only one particle is shifted within the sea, the other particle being expelled from the sea and described in its final state by the semi-internal correlation functions $\hat{f}_{ij;l}$ (see the figures in Paper I). The original perturbation approach has been generalized by Sinanoğlu[20] and co-workers to the nonperturbative theory[21-23] outlined in I. In addition to the already described internal and semi-internal correlations there remain the all-external correlations similar to those which occur in the closed-shell case.[19] However, the single-particle all-external correlations in open shells are not negligible as are their counterparts in closed shells. These now include the so-called orbital and spin polarization effects.[19] The remaining all-external correlations, however, as in the closed-shell case, are very well described in terms of pair correlation functions $\hat{U}'_{ij}$ and unlinked products of such functions. The analysis presented in I and II shows that the correlations may be regrouped into three types which are quite independent of each other:

$$\psi=\Phi_{\mathrm{RHF}}+\chi_{\mathrm{INT}}+\chi_f+\chi_u\ , \tag{11}$$

$$\Phi_{\mathrm{RHF}}=\sum_{K=1}^{\mathcal{K}}C_K\Delta_K\ , \tag{12a}$$

$$\chi_{\mathrm{INT}}=\sum_{K=\mathcal{K}+1}^{\binom{M}{N}}d_K\Delta_K\ , \tag{12b}$$

$$\chi_f=\sum_{K=1}^{\mathcal{K}}C_K\chi_f^{K}=\sum_{K=1}^{\mathcal{K}}C_K\,\mathcal{A}(N)(k_1\cdots k_N)$$

$$\times\left(\sum_{i}\frac{\hat{f}^{K}_{k_i}}{(k_i)}+\sum_{\substack{i<j\\ l\notin K}}\frac{{}^{l}\hat{f}^{K}_{k_ik_j;l}}{(k_ik_j)}+\cdots\right), \quad (12c)$$

$$\chi_u=\sum_{K=1}^{\mathcal{K}}C_K\chi_u{}^K=\sum_{K=1}^{\mathcal{K}}C_K\,\mathcal{A}(N)(k_1\cdots k_N)$$

$$\times\left(\frac{1}{2^{1/2}}\sum_{i<j}\frac{\hat{U}'^{K}_{k_ik_j}}{(k_ik_j)}+\text{unlinked clusters}\right). \quad (12d)$$

Φ_{RHF} is a linear combination of $\mathcal{K}$ determinants Δ_K each formed with N orbital subsets $k_1k_2\cdots k_N$ of the M Hartree-Fock orbitals. Excitations from these occupied orbitals to other orbitals within the sea (i.e., internal correlations) lead to the expansion of χ (internal) in terms of the remaining $\binom{M}{N}-\mathcal{K}$ determinants constructed with $\varphi_1\cdots\varphi_M$. The $\hat{f}_{k_a}{}^K$ is an orbital polarization correlation function and

$$\hat{f}^{K}_{k_ik_j;l}$$

is a semi-internal correlation function describing the final state of the particle expelled from the sea after the collision of electrons in orbitals k_i and k_j results in the other being excited to the previously vacant orbital l. Two-body, all-external correlations depicted by $\hat{U}_{k_ik_j}{}'^K$ are the main correlations common to both open and closed shells. All these correlation functions are discussed in much more detail in I. Finally we note that all these correlation functions are orthogonal to each orbital within the HF sea and that

$$\langle\Phi_{\mathrm{RHF}}|\psi\rangle=\langle\Phi_{\mathrm{RHF}}|\Phi_{\mathrm{RHF}}\rangle\equiv1. \quad (13)$$

The correlations in χ_{INT} and χ_f, which includes semi-internal and polarization effects, are highly specific to the state under consideration, depending upon N, Z, and the symmetry of the state. These so-called nondynamical correlations are thus not transferable from one state to another; however, as shown in I, they are amenable to a *finite* configuration interaction (CI) expansion. The determinants entering into this expansion are limited by symmetry and have either all N of their orbitals within the HF sea (internal correlation) or at most one orbital chosen from outside the M orbital sea (polarizations and semi-internal correlations). These nondynamical correlations can significantly modify the RHF charge distribution and thus play a very influential role in the calculation of oscillator strengths. The correlations depicted by χ_u, on the other hand, being the same as those occurring in the closed-shell states, should have little effect upon the charge density in the outer regions of the atom and thus contribute little to modifications in the RHF values of f_R and f_∇. Although the dynamical correlations in χ_u can be calculated by the methods discussed by Silverstone and Sinanoğlu,[19] the procedure is much more difficult than the finite CI technique suitable for finding the nondynamical correlations. In particular, no finite CI expansion will yield all the dynamical correlation effects. The salient hypothesis resulting from the NCMET analysis is that the correlations essential to the computation of accurate oscillator strengths, are only the two nondynamical types of correlations. The "semi-internal effect" shown below to be important for transition probabilities has not been considered as a distinct and significant effect in the previous literature.

IV. METHOD OF CALCULATION

We have calculated the multiplet absorption oscillator strengths f_R, f_∇, and f_A with the detailed wave functions described in I for the various configurations $1s^22s^m2p^n(0\leq m\leq2, 0\leq n\leq6)$ of atoms and ions with nuclear charge $5\leq Z\leq11$. These wave functions contain all the nondynamical correlation effects among L-shell electrons. The correlations of the K-shell electrons are predominantly dynamical because of the relatively large energy separation between the $1s$ orbital and the vacant orbitals in the HF sea. In addition, we also calculated these oscillator strengths using the RHF wave functions as well as with wave functions which contain only selected parts of the nondynamical correlations. Each of these approximate wave functions can be expanded as a finite linear combination of Slater determinants Δ_K constructed from N-single-particle functions selected from an orthonormal set of Q orbitals $\varphi_1\cdots\varphi_M\varphi_{M+1}\cdots\varphi_Q$. The first M orbitals define the HF sea and the remaining $Q-M$ orbitals are used to expand $\hat{f}^K_{k_ik_j;l}$. For example, the MET wave function containing all nondynamical correlations can be written

$$\Psi_{\mathrm{nondyn}}=\Phi+\chi_{\mathrm{INT}}+\chi_f=\sum_{K=1}^{\mathcal{K}}C_K\Delta_K$$

$$+\sum_{K=\mathcal{K}+1}^{\binom{M}{N}}d_K\Delta_K+\sum_{K=\binom{M}{N}+1}^{\binom{M}{N}+\sigma}C_K{}^F\Delta_K\,. \quad (14)$$

The $\sigma=\binom{M}{N-1}(Q-M)$ determinants needed to expand χ_f contain $N-1$ orbitals from the set $\varphi_1\cdots\varphi_M$ and one chosen from among the remaining $Q-M$ orbitals. The number of nonvanishing terms in (14) is limited by symmetry restrictions.

For the states considered here the spin orbitals associated with $1s$, $2s$, and $2p$ electrons ($M=10$) make up the HF sea and the complementary set is represented by 32 spin orbitals of symmetries labeled $3s$, $3p$, $3d$, and $4f$. For all states γLSM_LM_S, all 42 single-particle functions have the form

$$\varphi_i = R_{n_i l_i}(r)\, Y_{l_i}^{m_i}(\vartheta, \varphi) X_{m_{s_i}}(\sigma_z)\ , \qquad (15)$$

where Y and X are the normalized spherical harmonics and spin functions. The radial functions corresponding to a given spin orbital were determined independently for each γ, L, S so that the overlap between orbitals φ_i and φ_j' associated with states γLS and $\gamma'L'S'$ is

$$\int \varphi_i^*(x)\varphi_j'(x)\,dx = \int_0^\infty dr\, r^2 R(r)_{n_i l_i} \times R'(r)_{n_j l_j}\, \delta_{l_i l_j}\, \delta_{m_i m_j}\, \delta_{m_{s_i} m_{s_j}}\ . \qquad (16)$$

We explicitly took the "nonorthogonality" of these orbitals into account in evaluating the N-body integrals

$$(\Psi_{\gamma LSM_LM_S} \,|\, O_i \,|\, \Psi_{\gamma'L'S'M_L'M_S'}) = \sum_K \sum_{K'} C_K C'_{K'} \times \int dx_1 \cdots dx_N\, \Delta_K^*(x_1 \cdots x_N) \times O_i\, \Delta'_{K'}(x_1 \cdots x_N)\ . \qquad (17)$$

Thus the frozen-core approximation[1,9-11] is abandoned in favor of a rigorous evaluation of these N-electron integrals. This is reflected in our RHF calculations where, for example, our results are roughly 0.98 times those of Kelley[11] for some transitions in the ions of nitrogen and oxygen. The usual procedure for attacking the nonorthogonality problem – the co-factor method[24] – was replaced with a method put forth by King *et al.*[25] The problem as it occurs in the oscillator-strength calculation allows some even further refinements of their method which are presented in the Appendix.

All the approximate wave functions are constructed to be eigenfunctions of $\hat{L}^2$, $\hat{S}^2$, $\hat{L}_z$, and $\hat{S}_z$. Indeed it is natural to try to incorporate in the approximate functions as many of the symmetry properties of the exact wave function as possible. This seems especially important when computing off-diagonal matrix elements. In addition, the symmetry constraints bring about tremendous simplifications emerging from group theoretical considerations of these matrix elements.[26] The operators $\vec{R}$, $\vec{\nabla}$, and $\vec{A}$ are scalars in spin space and rank-one tensors in position space. Therefore the familiar electric dipole selections rules $\Delta S=0$, $\Delta M_S=0$, $\Delta L=0,\pm 1$, $\Delta M_L=0,\pm 1$ follow immediately, where $\Delta S = S - S'$, etc., and the nonvanishing matrix elements are independent of $M_S (= M_{S'})$. Moreover, given γLS and γ', $L' (=L-1, L, L+1)$, $S' (=S)$, every nonvanishing matrix element of the operators $O_1 = \vec{R}$, $O_2 = \vec{\nabla}$, $O_3 = \vec{A}$, can be expressed in terms of a single parameter $\beta_i(\gamma LS; \gamma'L'S')$ ($i = 1, 2, 3$ corresponding to the operator O_i) multiplied by expressions involving only L, M_L, and $M_{L'}$.[3] Note in particular that the parameter is independent of the quantum numbers M_L, $M_{L'}$, M_S, and $M_{S'}$, the summation indices occurring in (4), (5), and (6). Consequently the expressions for the multiplet line strength may be written as the product of the parameter $\beta_i(\gamma LS; \gamma'L'S')$ by a simple algebraic function of L and S resulting from the summations. Finally, notice only one nonvanishing matrix element need be evaluated to determine $\beta_i(\gamma LS; \gamma'L'S')$, so that instead of computing all the matrix elements occurring in the sums (4), (5), or (6) a single matrix element (for each O_i) suffices to find the line strength for given γLS, $\gamma'L'S'$.

All the computations were carried out on an IBM 7094/7040 DCS computer in which the wave functions of Sinanoğlu and Öksüz form the input data.[1] The program first computes all the nonvanishing one-body integrals

$$\int \varphi_i^*(x)\varphi_j'(x)\,dx, \quad \int \varphi_i^*(x)\vec{r}\varphi_j'(x)\,dx,$$
$$\int \varphi_i^*(x)\,\vec{\nabla}\varphi_j'(x)\,dx, \quad \int \varphi_i^*(x)\frac{1}{r^2}\,\frac{\vec{r}}{r}\,\varphi_j'(x)\,dx,$$

which are needed, taking into account the symmetry restrictions (16) for the overlap and the selection rules[5] $\Delta l = \pm 1$, $\Delta m_l = 0, \pm 1$, $\Delta m_s = 0$ for the vector operators. The sum in (17) is then evaluated term by term using these integrals in the nonorthogonality procedure outlined in the Appendix. A calculation of f_R, f_∇, and f_A using all three types (Φ_{RHF}, $\Phi_{\mathrm{RHF}} + \chi_{\mathrm{INT}}$, and $\Phi_{\mathrm{RHF}} + \chi_{\mathrm{INT}} + \chi_f$) of wave functions for each (i.e., nine values in all are computed) requires about thirty seconds of computer time.

V. RESULTS AND DISCUSSION

The multiplet absorption oscillator strengths for 29 ultraviolet transitions ($1s^22s^22p^n \rightarrow 1s^22s2p^{n+1}$) in the species C II, N I, N II, N III, O II, O III, O IV, F II, Ne II, and Na III are presented in Table I. In column two we list the oscillator strengths found in the National Bureau of Standards (NBS) Tables[2] of May 1966. The next six columns contain results of the present study. Columns three and

TABLE I. Multiplet absorption oscillator strengths for 29 ultraviolet $1s^22s^22p^n \rightarrow 1s^22s2p^{n+1}$ transitions obtained with the dipole-length and -velocity operators using RHF and MET wave functions.

Transition	f^{NBS}	f_R^{RHF}	f_∇^{RHF}	$f_{(R\nabla)^{1/2}}^{\mathrm{RHF}}$	f_R^{MET}	f_∇^{MET}	$f_{(R\nabla)^{1/2}}^{\mathrm{MET}}$	$f^{\mathrm{Experiment}}$
C II $2p\,^2P \rightarrow 2p^2\,^2D$	0.27	0.263	0.262	0.262	0.125	0.134	0.129	0.114^{29} (10%)
N III $2p\,^2P \rightarrow 2p^2\,^2D$	0.18	0.213	0.214	0.213	0.114	0.125	0.119	0.103^{30} (10%)
O IV $2p\,^2P \rightarrow 2p^2\,^2D$	0.15	0.179	0.181	0.180	0.106	0.111	0.108	0.091^{31} (3%)
C II $2p\,^2P \rightarrow 2p^2\,^2S$	0.059	0.070	0.042	0.054	0.122	0.121	0.121	
N III $2p\,^2P \rightarrow 2p^2\,^2S$	0.11	0.056	0.035	0.044	0.085	0.084	0.084	
O IV $2p\,^2P \rightarrow 2p^2\,^2S$	0.10	0.047	0.030	0.038	0.069	0.071	0.070	
C II $2p\,^2P \rightarrow 2p^2\,^2P$	0.52	0.736	0.282	0.456	0.501	0.471	0.486	
N III $2p\,^2P \rightarrow 2p^2\,^2P$	0.45	0.577	0.227	0.362	0.399	0.390	0.394	0.416^{30} (18%)
O IV $2p\,^2P \rightarrow 2p^2\,^2P$	0.38	0.473	0.189	0.299	0.334	0.329	0.331	
N II $2p^2\,^3P \rightarrow 2p^3\,^3D$	0.17	0.236	0.268	0.251	0.100	0.105	0.102	0.109^{29} (11%) 0.101^{30} (6%)
O III $2p^2\,^3P \rightarrow 2p^3\,^3D$	0.15	0.200	0.225	0.212	0.100	0.104	0.102	0.102^{31} (3%)
N II $2p^2\,^3P \rightarrow 2p^3\,^3P$	0.22	0.170	0.138	0.153	0.137	0.155	0.146	0.131^{30} (6%)
O III $2p^2\,^3P \rightarrow 2p^3\,^3P$	0.18	0.143	0.117	0.129	0.127	0.135	0.131	
N II $2p^2\,^3P \rightarrow 2p^3\,^3S$	0.23	0.334	0.110	0.192	0.218	0.203	0.210	0.189^{30} (9%)
O III $2p^2\,^3P \rightarrow 2p^3\,^3S$	0.19	0.272	0.092	0.158	0.183	0.173	0.178	
N II $2p^2\,^1D \rightarrow 2p^3\,^1D$	0.45	0.651	0.310	0.449	0.314	0.327	0.320	
O III $2p^2\,^1D \rightarrow 2p^3\,^1D$	0.37	0.534	0.263	0.375	0.297	0.303	0.300	
N II $2p^2\,^1D \rightarrow 2p^3\,^1P$	0.30	0.245	0.094	0.152	0.298	0.261	0.279	
O III $2p^2\,^1D \rightarrow 2p^3\,^1D$	0.25	0.202	0.080	0.127	0.219	0.193	0.206	
N II $2p^2\,^1S \rightarrow 2p^3\,^1P$	0.40	0.817	0.457	0.611	0.259	0.309	0.283	
O III $2p^2\,^1S \rightarrow 2p^3\,^1P$	0.35	0.669	0.388	0.509	0.294	0.337	0.315	
N I $2p^3\,^4S \rightarrow 2p^4\,^4P$	0.13	0.503	0.542	0.522	0.145	0.176	0.160	0.080^{29} (10%) 0.13^{27}
O II $2p^3\,^4S \rightarrow 2p^4\,^4P$	0.43	0.428	0.457	0.442	0.206	0.225	0.215	0.182^{31} (3%)
O II $2p^3\,^2D \rightarrow 2p^4\,^2D$	0.25	0.263	0.189	0.223	0.141	0.167	0.153	
O II $2p^3\,^2P \rightarrow 2p^4\,^2S$	0.15	0.125	0.081	0.101	0.097	0.102	0.099	
O II $2p^3\,^2P \rightarrow 2p^4\,^2D$	0.07	0.126	0.122	0.124	0.030	0.043	0.036	
F II $2p^4\,^3P \rightarrow 2p^5\,^3P$	0.56	0.322	0.263	0.291	0.140	0.172	0.155	
Ne II $2p^5\,^2P \rightarrow 2p^6\,^2S$	0.33	0.176	0.117	0.143	0.073	0.091	0.082	$0.035^{28} > 0.055$[a]
Na III $2p^5\,^2P \rightarrow 2p^6\,^2S$		0.155	0.105	0.128	0.077	0.090	0.083	

[a] Unpublished work of G. M. Lawrence and J. Hesser; see Ref. 28.

four list the results obtained with RHF wave functions using the dipole-length and dipole-velocity operators, respectively. The results of similar calculations using the MET wave functions containing all nondynamical correlation effects are presented in columns six and seven. In the RHF and MET calculations the energies used were computed as the expectation value of the Hamiltonian with respect to the corresponding wave function. Thus each is a "completely theoretical" calculation. The dependence of the oscillator strengths upon the calculated energy can be explicitly eliminated by taking the root-mean-square value of f_R and f_∇. These values for the RHF and MET wave functions are presented in columns five and eight, respectively. The final column lists the available experimental data and their uncertainty.

Since all the transitions reported here lie in the far-ultraviolet region, experimental determinations of the multiplet oscillator strengths are very difficult, and only recent advances have made any measurements possible. With the exception of Labuhn's results[27] for N I and Hinnov's results[28] for Ne II, the experimental multiplet absorption oscillator strengths reported in Table I were computed from lifetime measurements of the excited states in the inverse decay processes. The values of Lawrence and Savage[29] for N I and N II were obtained with the phase-shift method, while those of Heroux[30] for N II and N III and Bickel[31] for O II, O III, and O IV were obtained with the beam-foil technique. The methods generally yield results accurate to within 10–20%; the uncertainties reported in Table I for each individual measurement are based on the experimental error in the measured lifetime reported by the authors.

Bickel is not certain that he has actually measured the lifetime of the $^4P \rightarrow {}^4S$ decay in O II used to compute f^{Exp} in Table I, for this transition at $\lambda = 833.0$ Å is difficult to resolve from the $^3D \rightarrow {}^3P$ transition in O III at $\lambda = 834.5$ Å which is surely present. If this O II transition is actually observed then both transitions have the same lifetime of $1.7\ (\pm 0.04) \times 10^{-9}$ sec. Labuhn's value for N I was obtained from an emission experiment carried out with a wall-stabilized arc. Hinnov's result for Ne II is found from fitting light-intensity and ion-density measurements on a neon plasma to an expression containing the oscillator strengths for many transitions as adjustable parameters. There seems a great possibility that Hinnov's value may be in error, as he notes in Sec. IV of his paper where he also refers to an unpublished result of Lawrence and Hesser which contradicts his reported value.

The agreement between the experimental data and the corresponding MET values is an encouraging confirmation of the theory, particularly in light of the substantial role correlation effects play in determining these oscillator strengths. With but two exceptions – the $^4S \rightarrow {}^4P$ transition in N I and the $^2P \rightarrow {}^2S$ transition in Ne II – our values of the root mean square of f_R and f_∇ are within 20% of the available experimental results which are themselves sometimes subject to equal uncertainties. Often our values are in even better agreement with experiment, the average deviation of our results from the experimental ones being only 11%. It is particularly interesting to note that for the two exceptional cases mentioned above there are alternative, contradictory sets of experimental data.[27–29] In both instances the MET calculations make an unambiguous preference for the higher values, although a redetermination of f for N I ($^4S \rightarrow {}^4P$) by Lawrence (private communication) agrees with his earlier result which is roughly one-half the MET value. The MET values obtained here may be used with considerable confidence for that majority of transitions where no experimental corroboration yet exists. This confidence is based on the theoretical analysis predicting the importance of nondynamical correlation effects and is bolstered by the agreement obtained with the overwhelming majority of experiments reported in Table I. Thus it is hoped that our MET values will be of immediate use in atomic and astrophysical applications.

The influence of the nondynamical correlations is felt substantially in virtually all the cases considered. Changes in the computed oscillator strengths by factors of 2–3 due to correlation effects are not uncommon. With but few exceptions we find $f_R^{\mathrm{RHF}} > f_R^{\mathrm{MET}}$, i.e., the RHF calculations usually – but not always – overestimate f_R. The exceptions point out the highly specific character of the effects introduced by the nondynamical type correlations. Similar trends are, of course, encountered among the same transitions in species differing in only their nuclear change. In addition, our results underscore the fact that agreement between f_R and f_∇ obtained with RHF wave functions does not insure their accuracy.[10,14] In more than one case we find that although $f_R^{\mathrm{RHF}} \approx f_\nabla^{\mathrm{RHF}}$, these values are drastically changed upon introducing the nondynamical type correlations. The $^2P \rightarrow {}^2D$ multiplet in C II is a clear illustration of this point. There are, of course, many more instances in which f_R^{RHF} and f_∇^{RHF} do *not* agree, as exemplified in the $^2P \rightarrow {}^2P$ transitions in C II. Often they differ by a factor of 2–3. On the other hand, the agreement between f_R^{MET} and f_∇^{MET} is *consistently* good, usually within 15%. Therefore the root-mean-square values computed with the MET wave functions do not differ significantly from either the corresponding dipole-length or dipole-velocity results. While on this point let us note that in general the root-mean-square values obtained with RHF wave functions do not agree with the MET results nor with experiment. Exceptional cases in which f_R^{RHF} and f_∇^{RHF} significantly disagree with one another but yield reasonably accurate root-mean-square values are found for the $^3P \rightarrow {}^3S$ (N II and O III) as well as the $^2P \rightarrow {}^2S$ (O II) transitions. Nevertheless, it is clear from Table I that the arguments advanced by Hansen[8] for trusting the root-mean-square values of f_R^{RHF} and f_∇^{RHF} for transitions involving no near degeneracies cannot in general be extended to transitions considered here.

We have also calculated the oscillator strengths using the acceleration operator. Although the outlandishly large values obtained with the RHF wave functions are substantially reduced when the nondynamical correlations are added, a very large discrepancy still remains between f_A^{MET} and f_R^{MET}, f_∇^{MET}, or experiment. La Paglia[32] has pointed out that it is appropriate for additional terms to be included in the dipole-acceleration operator when calculating with RHF wave functions. These terms arise from the commutator of $\vec{\nabla}$ and the nonlocal Hartree-Fock Hamiltonian which replaces the exact Hamiltonian in order to take advantage of the eigenfunction character of the approximate wave functions. No such correction terms appear, of course, in an exact formulation, and thus we have not included them in our acceleration operator calculations. Their inclusion might be helpful but surely would be artificial in our calculations. The discrepancy in f_A^{MET} must therefore be attributed to the failure of the wave functions to include the important correlation effects in the region most sensitive to the acceleration operator. Indeed, this is the innermost shell in which the correlation is predominantly dynamical or "all-external" and thus not included in the MET wave functions used in

TABLE II. A representative sample of multiplet absorption oscillator strengths obtained with dipole acceleration as well as dipole-length and -velocity operators using RHF and MET wave functions.

Transition	f_R^{RHF}	f_∇^{RHF}	f_A^{RHF}	f_R^{MET}	f_∇^{MET}	f_A^{MET}
C II ${}^2P \to {}^2D$	0.263	0.262	41.7	0.125	0.134	9.64
O IV ${}^2P \to {}^2S$	0.047	0.030	3.86	0.069	0.071	1.87
N II ${}^3P \to {}^3P$	0.170	0.138	18.0	0.137	0.155	5.61
N II ${}^1D \to {}^1P$	0.245	0.094	5.33	0.298	0.261	3.09
O II ${}^4S \to {}^4P$	0.428	0.457	84.6	0.206	0.225	15.9

the present calculation. In Table II we present some typical results obtained with the dipole-acceleration operator for both RHF and MET wave functions and include the previously tabulated f_R^{MET}, f_∇^{MET}, f_R^{RHF}, and f_∇^{RHF} for comparison.

The need for considering correlation effects in treating transitions involving equivalent electrons has been recognized for many years. Early investigations by Bolotin, Levison, Levin, and Yustis were based on the "double-configuration" approximation in which only two determinants were mixed to expand the lower state involved in the transition.[33–35] Similar approaches can be found in the pioneering work of Trefftz[36] on Mg I and Ca I as well as his later calculations[37] on iron and Be-like ions. Layzer[38] has developed a theory based on the sets of determinants called complexes. Each complex consists of all isosymmetric determinants formed with configurations which would be degenerate in a one electron model based on hydrogenic orbitals. Froese[39] and Varvasky[40] have carried out configuration mixing in "zero order" which includes only the complex composed of determinants degenerate with the Restricted Hartree-Fock configuration of the lower term. A similar approach has been taken by Dalgarno and his co-workers.[41] All these calculations include at best only what we have described above as the internal correlation effects. Often these are not even included in their entirety. While in most instances these calculations represent an improvement on the RHF results, quantitative agreement with experiment is seldom achieved. Other correlation effects – in particular, the remaining nondynamical correlations introduced in the present theory[1] – must also be included in calculating f_R and f_∇.

To illustrate the necessity of including all nondynamical correlations, we present in Table III the results of four types of calculations on eight representative transitions: The 2nd column lists our f_R^{RHF}, our Restricted Hartree-Fock results. Successive columns list results obtained after the introduction of one or more specific types of nondynamical correlations: f_R^{CD} denotes the results of Cohen and Dalgarno[41] who introduce internal correlation into the lower states by mixing configurations degenerate with the RHF wave function. [$\chi\,(\text{internal}) \equiv 0$ for the upper states of transitions listed in Table III.] f_R^{INL} denotes another of our calculations in which, while internal correlations alone were introduced into the lower states, the upper states contained all possible nondynamical correlations. The second last column tabulates f_R^{MET} con-

TABLE III. Comparison of multiplet absorption oscillator strengths for transitions between states in which various parts of the nondynamical correlations are included. [RHF ≡ results obtained with restricted Hartree-Fock wave functions for initial and final states; CD ≡ Cohen and Dalgarno's results which include at best the internal correlations in the lower states; INL ≡ results obtained with internal correlations considered in the lower states while polarization effects and semi-internal correlations are introduced into the upper states; MET ≡ results obtained with present theory (Sinanoğlu, Öksüz, Westhaus).]

Transition	f_R^{RHF}	f_R^{CD}	f_R^{INL}	f_R^{MET}	$f^{\text{Experiment}}$
C II ${}^2P \to {}^2D$	0.263	0.204	0.121	0.125	0.114[29]
N II ${}^3P \to {}^3D$	0.236	0.192	0.097	0.100	0.109[29] 0.101[30]
N II ${}^3P \to {}^3P$	0.170	0.213	0.175	0.137	0.131[30]
N II ${}^3P \to {}^3S$	0.334	0.244	0.226	0.218	0.189[30]
N III ${}^2P \to {}^2D$	0.213	0.167	0.114	0.114	0.103[30]
N III ${}^2P \to {}^2P$	0.577	0.415	0.404	0.399	0.416[30]
O III ${}^3P \to {}^3D$	0.200	0.162	0.099	0.100	0.102[31]
O IV ${}^2P \to {}^2D$	0.179	0.141	0.105	0.106	0.091[31]

taining all nondynamical correlations in both terms, while the experimental values are displayed in the last column. Comparing $f_R{}^{\mathrm{RHF}}$ and $f_R{}^{\mathrm{CD}}$ we conclude that the internal correlations in the ground state do play a major role. With but one exception the results of Cohen and Dalgarno do correct the RHF values in the right directions. Furthermore, when the semi-internal and polarization corrections are introduced only into the upper state – that is, internal effects alone are considered in the lower state – agreement with the full MET calculations is often very good. Note, however, that when the internal correlations are suppressed by symmetry as they are in the upper state, the remaining nondynamical type correlations *must* be included to obtain the quantitative agreement with experiment. (Compare $f_R{}^{\mathrm{CD}}$ and $f_R{}^{\mathrm{INL}}$ with $f_R{}^{\mathrm{MET}}$ and experiment.) Thus the significant role played here by the internal correlations in the lower state does not diminish the importance of including other nondynamical effects in the calculations. The internal correlations are highly specific to transitions from the ground state. Indeed, in transitions from higher states, internal correlations (La Paglia's hole pair)[42] may be absent in which case the remaining nondynamical effects assume the entire burden of modifying the RHF results. Thus we conclude that *all* nondynamical type correlation as analyzed within the framework of MET must in general be included in the wave functions to obtain accurate oscillator strengths.

In predicting the configurations which must be mixed with Φ_{RHF} in order to compute f_R and f_∇ accurately, not only does MET provide the physical basis for our oscillator-strength calculations, but also it indicates the most efficient ways they may be carried out. For instance, large scale configuration interaction (CI) calculations in which no *a priori* attempt is made to separate the various types of correlation effects seem very inefficient if one's sole interest is in obtaining oscillator strengths. The configurations important for obtaining the *total* energy [see (Eq. 21) of Paper I] of the state – the criterion usually invoked in these CI calculations – include terms not necessarily relevant to determining accurate charge densities and thus accurate oscillator strengths. Such large scale CI expansions have recently been carried out by Weiss[7] for neutral and singly ionized carbon. His results for the $2p\ {}^2P \rightarrow 2p^2\ {}^2D$, $2p\ {}^2P \rightarrow 2p^2\ {}^2S$, and $2p\ {}^2P \rightarrow 2p^2\ {}^2P$ transitions in C II are in good agreement with our values. Weiss has included in addition to the internal and at least part of the remaining nondynamical correlations some of the all-external correlations which, according to our results, are not required. Since his excited-state wave functions are not reported it is not possible to say whether all the semi-internal and polarization correlation effects are accounted for, although the good agreement cited here suggests that they are included in large measure.

VI. CONCLUSION

The nonclosed-shell many-electron theory of atomic structure developed by Sinanoğlu and his co-workers incorporates electron correlations into the wave function in a systematic way. Of the three types which occur in open-shell states, the internal together with the semi-internal plus polarization correlations make up the highly specific, nondynamical parts which affect the charge distribution and consequently the oscillator strengths. These specific correlations may be computed independently of the shorter range dynamical ones. Wave functions containing all the nondynamical correlations (at least for the L shell) obtained in I for the $1s^2 2s^n 2p^m$ $(0 \leq n \leq 2,\ 0 \leq m \leq 6)$ configurations in atoms and ions with $5 \leq Z \leq 11$ have been used to calculate the absorption oscillator strengths for 29 ultraviolet transitions in C II, N I, N II, N III, O II, O III, O IV, F II, Ne II, and Na III. In most instances where the corresponding measurements are available our results for f_R and f_∇ compare very favorably with experiment; the average deviation of our root-mean-square values of f_R and f_∇ from the experimental ones is 11%.

Our results show that *all* the nondynamical correlation effects must be included to obtain accurate oscillator strengths. Most previous CI calculations mixed but very few configurations in only the ground state – e.g., the double configuration approximation – obtaining at best only part of what we have termed the internal correlations. On the other hand the large scale CI calculations fail to classify the types of correlation effects occurring in open-shell states and thereby include effects which are not necessarily of significance in the computation of f_R and f_∇. Of the three types which can occur, only the internal and semi-internal plus polarization correlations – that is, the nondynamical correlations – are important in finding approximate wave functions which accurately portray charge densities. The hypothesis that such wave functions should yield accurate values for f_R and f_∇ is borne out by our numerical results. To include all the nondynamical effects requires from 20 to 60 determinants depending upon the particular state. The calculations thus represent some of the most detailed oscillator-strength computations to date, while in the nonclosed shell MET theory they also have a physical basis.

The methods described herein can also be applied to higher-order electromagnetic interactions with atoms. In addition, Auger transitions may also be treated in a similar manner with but slight modifications in our programs. The nondynamical correlation effects in transitions in the higher periods (e.g., transitions involving M and N shell equivalent electrons) can also be treated by the MET procedure. In extending our calculations to the heavier elements, however, it may be necessary to use a relativistic SCF based version of this theory.

ACKNOWLEDGMENTS

We extend our thanks to Dr. Öksüz for many helpful conversations throughout the course of this work. The financial assistance of the National Science Foundation and the Alfred P. Sloan Foundation in their grants to one of us (O. S.) is gratefully acknowledged. The other (P. W.) also thanks the Research Foundation of Oklahoma State University for financial assistance.

APPENDIX

To show the further simplifications that come about in applying the method of King, *et al.*[25] to the nonorthogonality problem in calculating oscillator strengths, we start with their Eq. (22)

$$\int dx_1 \cdots dx_N \Delta_K \hat{O} \Delta'_{K'} = \det\underline{U} \det\underline{V}^+ \times \sum_{i=1}^{N} \left\{ \sum_{j=1}^{N} \sum_{k=1}^{N} U^*_{ji} V_{ki} (\varphi^*_j | \hat{O} | \varphi'_k) \right\} \prod_{l \neq i}^{N} \hat{d}_{ll} , \tag{A-1}$$

where the $N \times N$ unitary $\underline{U}$ and $\underline{V}$ are chosen so that

$$\underline{U}^+ \underline{D} \underline{V} = \hat{\underline{d}} . \tag{A-2}$$

Here $\underline{D}$ is the overlap matrix between the orbitals in determinants Δ_K and $\Delta'_{K'}$. It may be shown that

$$\underline{U}^+ \underline{D} \underline{D}^+ \underline{U} = \underline{\Lambda} , \quad \underline{V}^+ \underline{D}^+ \underline{D} \underline{V} = \underline{\Lambda} , \tag{A-3}$$

where the eigenvalues are arranged so that $\lambda_1 \geqslant \lambda_2 \geqslant \cdots \lambda_N \geqslant 0$.

The selection rules for the one-body integrals

$$(\varphi_j | \hat{O} | \varphi'_k) = \int dx\, R^*_{n_j l_j} Y_{l_j}^{m^*_{l_j}} X^+_{m_{s_j}} \hat{O} R'_{n_k l_k} Y_{l_k}^{m_{l_k}} X_{m_{s_k}} \tag{A-4}$$

are $\Delta l = \pm 1$, $\Delta m_l = 0, \pm 1$, $\Delta m_s = 0$. Consequently, we need only consider a pair of determinants Δ_K and $\Delta'_{K'}$ for which

$$L_K = \sum_{k_i \in K} l_{k_i} \quad \text{and} \quad L'_{K'} = \sum_{k'_i \in K'} l_{k'_i}$$

differ by ± 1, and

$$M_K = \sum_{k_i \in K} m_{l_{k_i}} \quad \text{and} \quad M'_{K'} = \sum_{k'_i \in K'} m_{l_{k'_i}}$$

differ by $0, \pm 1$. Then, we have that

$$\det\underline{D} = \det\hat{\underline{d}} = 0 . \tag{A-5}$$

One can also show from the analysis of King, *et al.* that $|\hat{d}_{ii}| = \sqrt{\lambda_i}$ so that by our ordering of the eigenvalues λ_i and Eq. (A-5), we conclude $\hat{d}_{NN} = 0$. The outermost sum in Eq. (A. 1) reduces to a single term:

$$\int dx_1 \cdots dx_N \Delta_K \hat{O} \Delta'_K = \det\underline{U} \det\underline{V}^+ \prod_{l=1}^{N-1} \hat{d}_{ll} \times \left\{ \sum_{j=1}^{N} \sum_{k=1}^{N} U^*_{jN} V_{kN} (\varphi_j | \hat{O} | \varphi'_k) \right\} . \tag{A-6}$$

Note that the sums inside the curly brackets in (A-6) depend only on the components of the Nth column of U and V. Now we show that to evaluate the factor of these brackets the entire matrices $\underline{U}$ and $\underline{V}$ are not explicitly required but again only their Nth columns – that is the lowest eigenvectors of $\underline{D}\underline{D}^+$ and $\underline{D}^+\underline{D}$. The coefficient of the sums can be written

$$\begin{aligned} \det\underline{U} \det\underline{V}^+ \prod_{l=1}^{N-1} d_{ll} &= \det\underline{U} \det\underline{V}^+ \det \begin{bmatrix} \hat{d}_{11} & 0 & \cdots & 0 & 0 \\ 0 & \ddots & & & 0 \\ \vdots & & \ddots & \hat{d}_{N-1,N-1} & \vdots \\ 0 & & & & \\ 0 & 0 & \cdots & 0 & 1 \end{bmatrix} \\ &= \det\underline{U} \det\underline{V}^+ \det \left\{ \hat{\underline{d}} + \begin{bmatrix} 0 & 0 & \cdots & 0 \\ 0 & & & \vdots \\ \vdots & \cdot & \cdot & \cdot \\ 0 & \cdot & \cdot & 1 \end{bmatrix} \right\} \\ &= \det \left\{ \underline{U} \hat{\underline{d}} \underline{V}^+ + \underline{U} \begin{bmatrix} 0 & \cdots & 0 \\ \vdots & & \vdots \\ 0 & \cdots & 1 \end{bmatrix} \underline{V}^+ \right\} \end{aligned}$$

$$= \det\left\{\underline{D} + \begin{bmatrix} U_{1N}V^{+}_{N1} & \cdots & U_{1N}V^{+}_{NN} \\ \vdots & & \vdots \\ U_{NN}V^{+}_{N1} & \cdots & U_{NN}V^{+}_{NN} \end{bmatrix}\right\}$$

$$= \det\left\{\underline{D} + \begin{bmatrix} U_{1N}V^{*}_{1N} & \cdots & U_{1N}V^{*}_{NN} \\ \vdots & & \vdots \\ U_{NN}V^{*}_{1N} & \cdots & U_{NN}V^{*}_{NN} \end{bmatrix}\right\}$$

$$= \det \underline{D}' , \qquad \text{(A-7)}$$

with $D'_{ij} = D_{ij} + U_{iN} V^{*}_{jN}$. (A-8)

Thus to evaluate (A-6) we need the determinant of $\underline{D}'$ which in addition to the known elements $\underline{D}$ involves only the components of the Nth column of $\underline{U}$ and $\underline{V}$. The matrix diagonalization subroutine GIVENS very efficiently obtains just these components which, respectively, form the lowest eigenvectors of $\underline{D}\,\underline{D}^{+}$ and $\underline{D}^{+}\underline{D}$.

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PHYSICAL REVIEW VOLUME 183, NUMBER 1 5 JULY 1969

Correlation Effects of π Electrons. I. Screening[*]

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(Received 3 April 1969)

The screened potential in the π-electron system of large conjugated molecules is calculated by means of the random-phase approximation (RPA) method. The main qualitative feature of this potential is that at large distances one gets underscreening rather than screening. This and other properties of screening in such systems are discussed.

INTRODUCTION

This is the first in a series of papers on correlation effects in π-electron systems. Although the subject belongs to the area of chemical physics, and this paper might therefore seem more suitable for a more chemical journal, we wish to acquaint a broader group of physicists with an interesting finite Fermi system, to which one can apply the methods of many-body physics, and which has a rich phenomenology that can be compared and contrasted with other physical systems.

In this paper, we shall be mainly concerned with the effective interaction between two π electrons due to the modification of the direct interaction by the other π electrons. This is closely related to the problem of a test charge imbedded in the system. A procedure for calculating the screened potential of a test charge in a large conjugated molecule was described by one of us.[1] The test charge causes a redistribution of the π electrons in the molecule, which in turn modifies the potential field around the test charge. The calculation proceeds as follows: An external charge is artificially inserted into the molecule at the center of one of the benzene rings. A self-consistent-field molecular orbital (SCF MO) calculation is then performed for the molecule with the external charge, which yields the induced charges on the atomic sites. The net potential at any point is obtained as the sum of potentials due to the external charge and all the induced charges. The "bare" potential of the test charge is assumed to contain the average effect of the σ electrons, so that the resultant effective potential takes into account both σ- and π-electron screening. It is argued in Ref. 1 that this potential represents the effective interaction between two π electrons near the Fermi energy. The restriction to the neighborhood of the Fermi energy is due to the fact that the above procedure gives only the screened potential of a static impurity. In addition, since the system is inhomogeneous, the screening is different in various parts of the molecule. Therefore one has to calculate the effective potential of a test charge inserted at various places in the molecule. This by itself is very cumbersome, but even when this is done, the transition to the effective interaction between two electrons involves some uncertainty because the electrons are concentrated on atomic sites, while the test charge is in the middle of a benzene ring.

The method presented in this paper is based on the random-phase approximation (RPA) in a many-fermion system. We believe that this method is a better approximation than the one described above. It also enables us to calculate the dynamic effective interaction, which is essential for the investigation of the collective effects of the system. Moreover, this method gives us directly the values of the effective interaction $V(r_i, r_j, \omega)$ – for all atomic sites r_i and r_j in a single calculation.

The RPA method is equivalent to that of Gell-Mann and Brueckner, Sawada, and Hubbard[2] for the dense electron gas. Although our system is certainly not dense in the usual sense, we shall argue that the method is, nevertheless, applicable, since the basic condition for the applicability of RPA is that the interacting ground state differs only slightly from a filled Fermi sea. This is the case in a dense electron gas, and we shall show that this is also true in a large class of conjugated molecules.