where

$$z=\lambda e^{-\beta(R-R_0)}, \quad \lambda=(2/\beta)(2\mu D)^{1/2},$$

$$N_\nu=\frac{(\alpha-\nu-1)(\alpha-\nu-2)\cdots(\alpha-2\nu)}{\nu!\,\Gamma(\alpha-2\nu-1)}\,\beta,$$

$$F_\nu(z)=\sum_{s=0}^{\nu}\frac{(-1)^s\binom{\nu}{s}z^s}{(s-2\nu)(\alpha-2\nu+1)\cdots(\alpha-2\nu+s-1)},$$

where β is the parameter in Morse potential for the molecule

$$V(R)=D(e^{-2\beta(R-R_0)}-2e^{-\beta(R-R_0)}),$$

D is the dissociation energy, R_0 is the equilibrium separation, and μ is the reduced mass of the core. For H_2^+ a good choice[15] of parameters is

$$\beta=0.6678\ (\text{a.u.})^{-1}, \quad R_0=2.00\ (\text{a.u.}),$$

$$D=0.102\,65\ (\text{a.u.}), \quad \mu=918.334\ (\text{a.u.}).$$

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Theory of Atomic Structure Including Electron Correlation. IV. Method for Forbidden-Transition Probabilities with Results for [O I], [O II], [O III], [N I], [N II], and [C I].

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Electric quadrupole transition probabilities for the oxygen atom auroral line $^1S_0$–$^1D_2$ (λ = 5577 Å) and the ^2P–^2D, ^1S–^1D lines in C I, N I, N II, O II, and O III, which are of atmospheric and astrophysical interest, are calculated. The nonclosed-shell many-electron theory (NCMET) of atomic structure developed by Sinanoğlu and co-workers, which treats electron correlation accurately in both ground and excited states, predicts novel correlation effects which are included in the wave functions used to calculate the transition probabilities. These are many-body calculations on "forbidden" lines, the first of their kind. We explicitly examine the effect of electron correlation on the quadrupole line strengths. It is found that the Hartree-Fock values are reduced by 13–17% when all the important correlation effects are included in the wave functions. In view of the accuracy of the wave functions and of the method of calculation, the results obtained are expected to be accurate with a less than 5% uncertainty. For the much discussed O I $^1S_0$–$^1D_2$ (5577 Å) transition we find A_Q = 1.183 sec^{-1}. Comparison is made with previous experimental and theoretical work.

I. INTRODUCTION

In the first three papers of this series (Refs. 1–3, hereafter referred to as I, II, and III) a new nonrelativistic theory of atomic structure was developed and applied to 113 states of the $1s^22s^n2p^m$ ($0\le n\le 2$, $0<m\le 6$) configurations in atoms and ions with nuclear charge $5\le Z\le 11$.

The general theory for nonclosed-shell many-electron atoms and molecules was first derived by perturbation-variational methods by Silverstone and Sinanoğlu.[4] Novel correlation effects, not present in closed-shell species, were found to arise in nonclosed shells and in excited states and configurations. A nonperturbative theory was developed by Sinanoğlu and preliminary calculations on atoms were carried out in collaboration with Skutnik.[5] A systematic approach to the problem of atomic structure which requires the treatment of correlation effects in both ground and excited states was first given by Sinanoğlu and Öksüz.[1,2] A method of calculation of the different correlation effects was developed and computerized. More than a hundred states of B, C, N, O, F, Ne, and Na were examined and properties like electron affinities, excited states of negative ions, excitation energies, intermultiplet separations, and term-splitting ratios were calculated and compared favorably with experiment.

In III, Westhaus and Sinanoğlu,[3] using wave functions obtained in I and including the correlation effects indicated by the theory, calculated "allowed" electric dipole transition probabilities for a number of transitions of the type $1s^22s^22p^n \rightarrow 1s^22s2p^{n+1}$ in C II, N I, N II, N III, O II, O IV, F II, Ne II, and Na III. The agreement with recent accurate lifetime measurements was very good.

Recently,[5a] highly excited states of many-electron atoms lying in the discrete or the continuum spectrum have also been considered and their radiative transitions to the ground states have been calculated.

In this paper we present another application of the theory. "Forbidden" electric quadrupole transition probabilities are calculated for ^1S-^1D, ^2P-^2D lines in the C I, N I, N II, O I, O II, and O III ions important in astrophysics.

Previous results in the literature on forbidden lines were based on the independent-particle, central-field model, where only a single one-electron radial integral is calculated and then multiplied by an angular coefficient, a function of $(LSJ, L'SJ')$, to yield the line strengths and transition probabilities (for definitions see Sec. II). Two approximations, whose effect could not be estimated, were thus made. First, changes in the central field from term to term were often neglected and the same orbitals were used to describe all the terms of the same configuration (e.g., the same $2p$ orbital for the $1s^22s^22p^4\,{}^3P$, ^1D, ^1S terms). Secondly, and most important, electron correlation was neglected and its effect on the forbidden-transition probabilities could only be guessed at.[6,7] This was so because of the unavailability of a systematic theory of electron correlation until recently. In the present work we eliminate both approximations. We use the now available theory[1] of electron correlation mentioned above in ground and excited states to obtain detailed wave functions as described in I. In calculating the matrix elements of the electric quadrupole operator, N-body integrals are now computed and the nonorthogonality problem of the two sets (initial and final states) of one-electron functions is solved accurately in addition to the detailed inclusion of electron correlation. Our results reported here constitute the first study of this kind.

Measurement of forbidden-transition probabilities is extremely difficult, a real challenge to the experimentalist. Only for the O I $^1S_0-{}^1D_2$ auroral green line ($\lambda = 5577$ Å) there exist some but still not accurate experimental results. However, in view of the accuracy of the previous many-electron-theory results on energy properties as well as on allowed-transition probabilities, our hereby predicted values can be taken as rather accurate and used directly in atmospheric-astrophysical and atomic-physics applications.

II. PREVIOUS EXPERIMENTAL AND THEORETICAL RESULTS ON ELECTRIC QUADRUPOLE LINES

A. Oxygen $^1S_0$-$^1D_2$ Forbidden Line

The electric quadrupole line 5577 Å of the $^1S_0$-$^2D_2$ emission in the oxygen atom is a key spectral feature in the study of auroras. Atmospheric temperature measurements, possible mechanisms for the excitation and ionization of atoms and molecules, and possible electron and proton energy distributions in the atmosphere have their basis on observations of this line.[8–10] Furthermore, the line has recently been observed in the solar spectrum and measurements of its intensity have been used to determine the oxygen abundance in the sun.[11–13] Therefore, an accurate knowledge of the transition probability of this line is very useful.

Several measurements and calculations exist on the transition probability of the O I $^1S_0$-$^1D_2$ line.[14–21] However, the accuracies of the results remain in doubt at present.

Omholt[17] studied several types of rapidly changing auroras in which competitive factors, like collisional deactivation, vary. From his observations on the distribution of intensities in the various auroras, he suggested an upper limit for the lifetime of the upper state $^1S_0$ of $\tau = 0.75$ sec. The upper limit on the lifetime corresponds to the case of no collisional deactivation at all, so that the inverse of the lifetime is then just the sum of the transition probabilities for the $^1S_0$-$^3P_1$ (2972 Å) magnetic dipole and $^1S_0$-$^1D_2$ (5577 Å) electric quadrupole transitions. Taking the transition probability of $^1S_0$-$^3P_1$ to be[21] $A(2972\ \text{Å}) = 0.078\ \text{sec}^{-1}$, he calculated an average transition probability for the $^1S_0$-$^1D_2$ transition of $A(5577\ \text{Å}) = 1.43\ \text{sec}^{-1} \pm 14\%$.

LeBlanc *et al.*[14] have studied the emission of the four forbidden lines of the oxygen atom (5577 Å, 2972 Å, 6300 Å, and 6364 Å) from a discharge. Since the 5577-Å ${}^1S_0$-${}^1D_2$ and the magnetic dipole 2972-Å ${}^1S_0$-${}^3P_1$ lines have a common upper level, the ratio of their intensities should be equal to the ratio of the photon emission measured. They found this ratio to be $A(5577)/A(2972) = 22 \pm 2$, with no apparent dependence on the discharge conditions. The sum of these two transition probabilities is related to the radiative lifetime of the upper state by $A(5577) + A(2972) = \tau^{-1}$. Taking the lifetime of the ${}^1S_0$ state to be 0.7 ∓ 0.1 sec, the value measured by Omholt, they obtained the transition probabilities for the electric quadrupole ${}^1S_0$-${}^1D_2$ $A(5577) = 1.36 \pm 0.2$ sec^{-1} and for the magnetic dipole $A(2972) = 0.062 \pm 0.01$ sec^{-1}.

The ratio $A(5577)/A(2972)$ has also been measured by McConkey *et al.*[16] in the laboratory. Their value is $A(5577)/A(2972) = 18.6 \pm 3.7$. Recently, McConkey and Kernahan[15] measured an absolute transition probability by simultaneously measuring the number density N of the ${}^1S_0$ state and the intensity of the emitted radiation. In the same oxygen-helium discharge, the allowed ($\lambda = 1218$ Å) $(1s^2 2s^2 2p^4)$ ${}^1S$ – $(1s^2 2s^2 2p^3 3s)^1P$ vacuum uv absorption gave indirectly the N which was combined with the intensity measurement to obtain $A(5577) = 1.0$ sec^{-1}. However, the 50% uncertainty in the value of the ${}^1S$-${}^1P$ oscillator strength used, plus errors from statistical fluctuation (20%), absolute intensity measurements (10%), and discharge temperature (10%), make this result reliable only to within a factor of 2.[15]

The first theoretical prediction of the transition probability of the ${}^1S$-${}^1D$ line was made by Condon.[18] Using the general formulation of the theory of quadrupole radiation by Rubinowicz,[22] he developed formulas for the transition probabilities of electric quadrupole and magnetic dipole transitions in terms of matrix elements. The calculations were performed in the central-field approximation. In this approximation, the transition probability for the electric quadrupole transitions can be expressed as

$$A_Q(\alpha LSJ \rightarrow \alpha' L' S' J') = \delta(S, S') \frac{1679.2 \times 10^{15}}{(2J+1)\lambda^5} \times S_Q(\alpha LSJ \rightarrow \alpha' L' SJ') , \quad (1)$$

where A_Q is in sec^{-1}, λ is in Å, and S_Q, the line strength in atomic units, is given by

$$S_Q(\alpha LSJ \rightarrow \alpha' L' SJ') = F_Q(LSJ, L'SJ') s_q^2 . \quad (2)$$

Here, $F_Q(LSJ, L'SJ')$ is an angular factor characteristic of the particular line and determined by group theory, and s_q is the one-electron "electric quadrupole integral" defined by[23]

$$s_q = \tfrac{2}{5} \int_0^\infty dr\, r^2 P(np) P'(np) . \quad (3)$$

In modern terminology, using Racah tensors, Eq. (2) can be cast into a form[24]

$$S_q(\alpha LSJ \rightarrow \alpha' L' SJ') = \tfrac{2}{3} [R^Q_{\text{line}}(SLJ, SL'J')]^2 \times [R^Q_{\text{multiplet}}(\alpha L, \alpha' L')]^2 \times |\langle l \| \overleftrightarrow{C} \| l \rangle|^2 (\tfrac{5}{2})^2 s_q^2 . \quad (4)$$

The line factor R^Q_{line}, the multiplet factor $R^Q_{\text{multiplet}}$, and the reduced matrix element of the Racah tensor $\overleftrightarrow{C}$ with components

$$C_m^{(l)} = [4\pi/(2l+1)]^{1/2} Y_m^{(l)} \quad (5)$$

can be tabulated and thus transition probabilities in the central-field approximation can be given in terms of only the electric quadrupole integral s_q, as was done in Ref. 23.

Usually it is assumed that $R(np) = R'(np)$, the radial wave function of the ground state of the atom or ion, regardless of the actual states involved in a particular transition (e.g., ${}^1S_0$-${}^1D_2$ for O I). Of course, changes in the central field in going from ${}^1S_0$ to ${}^1D_2$ should affect the value of s_q. Condon, using Hartree wave functions[25] obtained $A(5577) = 2.0$ sec^{-1}. Pasternack,[19] using hydrogenlike wave functions with screening constants later obtained $A(5577$ Å$) = 2.2$ sec^{-1}. The most elaborate theoretical calculations of the radiative transition to date have been made by Garstang.[6,21,26] He used the numerical Hartree-Fock (HF) wave function of Hartree, Hartree, and Swirles[27] to obtain[21] $A = 1.28$ sec^{-1}. He later[6] included corrections for the configuration interaction in the upper state, considering only one perturbing term, however, the $2p^6\,{}^1S_0$, with the orbitals for the $1s$ and $2p$ electrons being the same as those of the $1s^2 2s^2 2p^4\,{}^1S_0$ configuration. His improved result is $A = 1.25$ sec^{-1}.

In the present paper we shall not use Eqs. (2)–(4). Instead of this "some one-electron central-field approximation," we shall obtain matrix elements between N-electron wave functions which include electron correlation as well as the different central fields.

B. C I ${}^1S$-${}^1D$, N I ${}^2P$-${}^2D$, N II ${}^1S$-${}^1D$, O II ${}^2P$-${}^2D$, and O III ${}^1S$-${}^1D$ Forbidden Lines

The electric quadrupole lines of C I, N I, N II, O II, and O III ions appear in the spectra of the airglow and auroras and of the gaseous nebulae and play an important role in their interpretation.[8,28] Like C I they may also prove useful for studies of element abundances in the sun and other stars.[11] There are no experimental results on the transition probabilities of these lines. Theoretical calculations have been done by Condon,[18] Pasternack,[19] Garstang,[21,29] Yilmaz,[30] and by Seaton and Osterbrock.[31] Hartree, hydrogenlike, variational "Morse"-type,[32] and HF wave functions were used in the adopted central-field approximation. Polarization and configuration-interaction (CI) corrections were not accounted for. Yilmaz's work takes into account some electron correlation. However, since his zero-order functions are not HF but simple analytical wave functions, the effectiveness of his method is difficult to estimate. Except for Seaton and Osterbrock who calculated s_q from the actual radial functions of the ^2P and ^2D terms, the other authors considered $R(2p) = R'(2p)$ the radial function of the ground state. Also the value of s_q reported in the N. B. S. tables for the N II ion was found by interpolation from the C I and O III values and not by direct calculation.[21] Due to the above approximations, an estimated error in the published values of up to 30% has been suggested.[6,7]

III. THEORY AND METHOD OF CALCULATION

The uncertainty of the few experimental results plus the approximations used in the previous theoretical calculations indicate the necessity of performing more elaborate calculations to obtain accurate results. Our many-body calculations take electron correlation explicitly into account. The problem of going beyond HF to include electron correlation is a formidable one if a straight CI approach is attempted. The CI method, being a series expansion, is of course in principle capable of giving the correct results. However, as noted by Garstang,[33] there is the crucial problem of which configurations to "mix" in order to obtain good wave functions suitable for calculations of transition probabilities. All configurations important for determining the energy are not of equal importance in computing transition probabilities which would seem to depend strongly only upon those configurations needed to specify an accurate charge distribution. The new atomic structure theory with electron correlation which we use, and the many-electron wave functions it yields as obtained in I, include certain theoretically predicted correlation effects completely. These affect the charge distributions the most. As in the case of the allowed-transition probabilities,[3,5a,34] they are expected to yield accurate results.

In the nonclosed-shell many-electron theory (NCMET) developed by Sinanoğlu and co-workers, the various kinds of correlation effects in excited as well as ground states are explicitly derived and taken into account.[1-5] Details on the theory can be found in Refs. 1, 2, and 4. We shall simply state the main features of NCMET and show how they are related to calculations of many-electron wave functions and transition probabilities.

The NCMET indicates three distinct types of correlation effects, each with a different type of dependence on the nuclear charge, the number of electrons, and the symmetry of the state. The theory shows that the exact N-electron wave function of an arbitrary (excited or ground) atomic state is of the form

$$\Psi = \phi_{\mathrm{RHF}} + \chi_{\mathrm{int}} + \chi_F + \chi_U , \tag{6}$$

with all parts orthogonal to one another and

$$\langle \phi_{\mathrm{RHF}} | \phi_{\mathrm{RHF}} \rangle = 1 . \tag{7}$$

Here ϕ_{RHF} is the nonclosed-shell restricted HF wave function which in general has the form

$$\phi_{\mathrm{RHF}} = \sum_{K \geq 1}^{\alpha} C_K \Delta_K , \tag{8}$$

where Δ_K is a Slater determinant. All the determinants in the sum belong to the same configuration of orbitals. χ_{int} ("internal") indicates virtual excitations in the "HF sea" to unoccupied orbitals in the sea.[35] This kind of correlation effect can be expressed in a finite CI:

$$\chi_{\mathrm{int}} = \sum_{K > \alpha}^{\binom{M}{N}} C_K \Delta_K , \tag{9}$$

where M is the number of HF-sea spin orbitals k_i, N is the number of electrons, and $\binom{M}{N}$ the binomial coefficient. For example, the well-known mixing of $1s^2 2s^2 2p^n \leftrightarrow 1s^2 2p^{n+2}$ in the first row, often used in configuration interaction studies of atomic spectra, belongs to χ_{int}. The χ_F includes the "semi-internal" correlations,[1] where at least one but not all electrons are "shifted" to other orbitals in the sea while the remaining ones are expelled from it. For example, given two electrons occupying the HF spin orbitals k_α, k_β in determinant Δ_K, one electron is excited into an empty sea orbital l (not belonging to Δ_k), while the other electron is expelled from the sea into a function $\hat{f}^{K}_{k_\alpha k_\beta ; l}(\vec{x}_2)$ such that

$$\langle \hat{f}^{K}_{k_\alpha k_\beta ; l}(\vec{x}_2) | m(\vec{x}_i) \rangle_{\vec{x}_2} = 0 , \tag{10}$$

where $m = 1, 2, \ldots, M$. χ_F also contains one-electron polarization $\hat{f}^{p}_{k_\gamma}$ of spin orbitals k_γ due to the noncentral field of the other electrons in nonspherically symmetric states. Finally, χ_U corresponds to all correlating electrons being expelled from the sea into pair functions $\hat{U}_{k_\alpha k_\beta}(\vec{x}_1, \vec{x}_2)$, with

$$\langle \hat{U}_{k_\alpha k_\beta}(\vec{x}_1, \vec{x}_2) | m(\vec{x}_2) \rangle_{\vec{x}_2} = 0 . \tag{11}$$

The first two correlation effects (χ_{int} and χ_F), 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. The $\hat{f}$ functions, giving the nondynamical correlations, could be obtained from the integrodifferential equations they satisfy, as shown in Ref. 4. However, they can also be calculated quite accurately by a *finite* configuration-interaction expansion. This is because, due to vector coupling restrictions imposed by the symmetry of the state, they contain only a finite number of spherical harmonics (e.g., in the $1s^2 2s^n 2p^m$ configurations only s, p, d, and f components). One thus has to determine only four new radial functions which are the new "semi-internal radial functions" of the theory. Here these are obtained variationally, using Slater-type orbitals whose exponent is optimized. Thus we obtain a set of $3s$-like, $3p$-like, $3d$-like, and $4f$-like orbitals which closely approximate the s, p, d, and f "semi-internal radial orbitals." Together with the HF orbitals, they constitute a finite orthonormal set, in terms of which the finite linear combination of internal, "semi-internal plus orbital polarization," i.e., χ_{int}, χ_F, and the ϕ_{RHF} determinants is formed and diagonalized to yield the "nondynamical" correlation energy and wave function.

The χ_U consists mainly of shorter range "dynamical" pair correlations which can be calculated by the methods discussed by Silverstone and Sinanoğlu.[4] A numerical method of solution has recently been developed by Winter *et al.* and applied to two-electron systems.[36] These correlations are the only ones remaining in the closed-shell systems. As discussed below, they are not important in calculating transition probabilities.

All three types are important in calculating energies and related quantities like electron affinities, term-splitting ratios, etc.[1,2] However, in calculating transition probabilities, only the internal, the semi-internal, and the polarization correlation effects are taken into account. This is because, in analogy with the closed-shell systems, the all-external correlations, due to their local shorter range character, do not affect the HF charge distributions appreciably. Therefore the RHF wave function along with the nondynamical correlations can most accurately describe the charge distributions and hence can be used to evaluate to high accuracy matrix elements of the transition operators. Therefore, in predicting the wave functions capable of yielding transition probabilities, the hypothesis is made that the all-external correlations are not important, a hypothesis borne out by the results on allowed electric dipole transitions.[3,5a,34] We shall call the wave functions to be used nondynamical or the "charge-distribution" (CD) wave functions:

$$\Psi_{\text{CD}} = \phi_{\text{RHF}} + \chi_{\text{int}} + \chi_F \, . \tag{12}$$

As mentioned above, such wave functions can be calculated by a finite and theoretically determined CI calculation with no ambiguity as to which configurations to choose. They 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.) They are given as a finite linear combination of Slater determinants Δ_K, constructed from N single-particle functions selected from an orthonormal set of Q orbitals $\phi_1 \cdots \phi_M \cdots \phi_Q$. The first $M = 10$ spin orbitals define the HF sea for the ground and low-lying states of the first row. The remaining $(Q-M)$ spin orbitals, the semi-internal orbitals, with at most four radial functions, are those that give the semi-internal $\hat{f}^{K}_{k_\alpha k_\beta; l}$ and polarization functions $\hat{f}^{p}_{l}$. They have the form, e.g.,

$$\hat{f}_{ij;k}(\vec{\mathrm{X}}) = f^{s}_{ij;k}(r)\, Y_{00} X_{m_s}(\sigma_z) + f^{p}_{ij;k}(r)\, Y_{1m_1} X_{m_s}(\sigma_z) + f^{d}_{ij;k}(r)\, Y_{2m_2} X_{m_s}(\sigma_z) + f^{f}_{ij;k}(r)\, Y_{3m_3} X_{m_s}(\sigma_z) \, , \tag{13}$$

where Y and X are the normalized spherical harmonics and spin functions. The $f^{l}_{ijk}(r)$ can be expanded as a sum of Slater-type orbitals (STO) but even one STO with an optimized exponent is quite sufficient.[1,2,5a]

In our calculation of transition probabilities we have used the general formulas given by Shortley.[37] The electric quadrupole transition probability is given by

$$A_Q(\alpha LSJ \to \alpha' L' S' J') = \frac{1}{2J+1} \, \frac{1679.2 \times 10^{15}}{\lambda^5} \times S_Q(\alpha LSJ \to \alpha' L' S' J') \, , \tag{14}$$

where A_Q is in $\sec^{-1}$, λ in angstrom units, and S_Q is the "line strength" defined by

$$S_Q(\alpha LSJ \to \alpha' L' S' J') = \sum_{M=-J}^{J} \; \sum_{M'_{J'}=-J'}^{J'} \left| \langle \alpha LSJM_J \,|\, \overleftrightarrow{\mathrm{Q}} \,|\, \alpha' L' S' M'_{J'} \rangle \right|^2 \tag{15}$$

and given in atomic units. The operator $\overleftrightarrow{\mathrm{Q}}$ is the quadrupole dyadic given by

$$\overleftrightarrow{\mathrm{Q}} = \sum_{i=1}^{N} \left(\vec{\mathrm{r}}_i \vec{\mathrm{r}}_i - \tfrac{1}{3} r_i^2 \overleftrightarrow{\mathrm{F}} \right)$$

where

$$\overleftrightarrow{\mathrm{F}} = \hat{i}\hat{i} + \hat{j}\hat{j} + \hat{k}\hat{k} \tag{16}$$

with the summation running over the electrons. As usual,

$$\left| \langle \alpha LSJM_J \,|\overleftrightarrow{\mathrm{Q}}|\, \alpha' L' S' J' M'_{J'} \rangle \right|^2 \equiv \langle \alpha LSJM_J \,|\overleftrightarrow{\mathrm{Q}}|\, \alpha' L' S' J' M'_{J'} \rangle$$

$$: \langle \alpha LSJM_J | \overleftrightarrow{Q} | \alpha' L'S'J'M'_{J'} \rangle^*, \tag{17}$$

where * = complex conjugate. As mentioned above, the many-electron wave functions are expanded as a linear combination of Slater determinants. They are given in the LSM_LM_S scheme.

Shortley[37] shows that $S_Q(\gamma J, \gamma' J')$ can also be written as

$$S_Q(\alpha LSJ \rightarrow \alpha' L'S'J') = f_q(LSJ\,;L'SJ')\,|\langle \alpha LS \| \overleftrightarrow{Q} \| \alpha' L'S' \rangle|^2 \delta(S,S')\,, \tag{18}$$

where

$$f_q(LSJ\,;L'SJ') = \tfrac{1}{16} \times [\text{coefficient of } G^2,\ H^2,\ I^2 \text{ of Condon and Shortley (Ref. 38)}]. \tag{19}$$

We calculate the reduced matrix element $\langle \alpha LS \| \overleftrightarrow{Q} \| \alpha' L'S \rangle$ as follows:

$$|\langle \alpha LS \| \overleftrightarrow{Q} \| \alpha' L'S \rangle|^2 = \delta(S,S')\,\delta(M_S, M'_{S'}) \frac{|\langle \Psi_{\alpha LSM_LM_S} | \overleftrightarrow{Q} | \Psi'_{\alpha' L'S'M'_{L'},M'_{S'}} \rangle|^2}{|[\langle \Psi | \Psi \rangle \langle \Psi' | \Psi' \rangle]^{1/2} \times \overleftrightarrow{G}(LM_L\,;L'M'_{L'})|^2} \tag{20}$$

$$= \frac{|\sum_n \sum_k a_n a_k \langle \Delta_n(M_L, M_S) | \overleftrightarrow{Q} | \Delta_k(M'_{L'}, M_S) \rangle|^2}{|(\sum_n a_n^2)^{1/2} (\sum_k a_k^2)^{1/2} \times \overleftrightarrow{G}(LM_L\,;L'M'_{L'})|^2}\,. \tag{21}$$

The general form of the tensor $\overleftrightarrow{G}(LM_L;\ L'M'_{L'})$ is given by the right-hand side of Eq. (3) of Ref. 39. Choose only two components of the dyadic, e.g., Q_{xx} and Q_{xz}. Then, for $M_L = M'_{L'}$ or $M_L = M'_{L'} \pm 2$, we obtain

$$|\langle \alpha LS \| \overleftrightarrow{Q} \| \alpha' L'S \rangle|^2 = \frac{|\sum_n \sum_k a_n a_k \langle \Delta_n(M_L, M_S) | Q_{xx} | \Delta_k(M'_{L'}, M_S) \rangle|^2}{|(\sum_n a_n^2)^{1/2} (\sum_k a_k^2)^{1/2} \times G_{xx}(LM_L;\ L'M'_{L'})|^2}\,, \tag{22}$$

where, for $M_L = M'_{L'}$,

$$|G_{xx}(LM_L;\ L'M'_{L'})|^2 = \tfrac{1}{6} \times \begin{cases} \tfrac{1}{6}[3M_L - L(L+1)]^2, & L = L' \\ \tfrac{3}{2}M_L^2(L - M_L)(L + M_L), & L = L' + 1 \\ \tfrac{3}{8}(L - M_L)(L + M_L)(L - 1 - M_L)(L - 1 + M_L), & L = L' + 2 \end{cases} \tag{23}$$

and for $M_L = M'_{L'} \pm 2$,

$$|G_{xx}(LM_L;\ L'M'_{L'})|^2 = \tfrac{1}{4} \times \begin{cases} \tfrac{1}{4}(L \pm M_L)(L \pm M_L - 1)(L \mp M_L + 1)(L \mp M_L + 2), & L = L' \\ \tfrac{1}{4}(L \pm M_L)(L \pm M_L - 1)(L \pm M_L - 2)(L \mp M_L + 1), & L = L' + 1 \\ \tfrac{1}{4}(L \pm M_L)(L \pm M_L - 1)(L \pm M_L - 2)(L \pm M_L - 3), & L = L' + 2. \end{cases} \tag{24}$$

Similarly, for $M_L = M'_{L'} \pm 1$, we have

$$|\langle \alpha LS \| \overleftrightarrow{Q} \| \alpha' L'S \rangle|^2 = \frac{|\sum_n \sum_k a_n a_k \langle \Delta_n(M_L, M_S) | Q_{xz} | \Delta_k(M'_{L'}, M_S) \rangle|^2}{|(\sum_n a_n^2)^{1/2} (\sum_k a_k^2)^{1/2} \times G_{xz}(LM_L;\ LM'_{L'})|^2}\,, \tag{25}$$

where

$$|G_{xz}(LM_L;\ LM'_{L'})|^2 = \tfrac{1}{4} \times \begin{cases} \tfrac{1}{4}(2M_L \mp 1)^2(L \pm M_L)(L \mp M_L + 1), & L = L' \\ \tfrac{1}{4}(L \mp 2M_L + 1)^2(L \pm M_L)(L \pm M_L - 1), & L = L' + 1 \\ (L - M_L)(L + M_L)(L \pm M_L - 1)(L \pm M_L - 2), & L = L' + 2. \end{cases} \tag{26}$$

The matrix element of Q_{xx} or Q_{xz} between two determinants Δ_n and Δ_k made of two orthonormal sets of one-electron functions

$$\varphi^{(n)}=\{\varphi_1^{(n)}, \varphi_2^{(n)}, \ldots, \varphi_N^{(n)}\}, \quad \varphi^{(k)}=\{\varphi_1^{(k)}, \varphi_2^{(k)}, \ldots, \varphi_N^{(k)}\} \tag{27}$$

is given by

$$\langle\Delta_n|Q_s|\Delta_k\rangle=\det\underline{U}\,\det\underline{V}^\dagger\sum_{i=1}^{N}\left(\sum_{j=1}^{N}\sum_{m=1}^{N}U_{ji}^{*}V_{mi}\langle\varphi_j^{(n)*}|q_s|\varphi_m^{(k)}\rangle\right)\prod_{l\neq i}^{N}\hat{d}_{ll}\ . \tag{28}$$

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

$$\underline{U}^\dagger\underline{D}\,\underline{V}=\hat{\underline{d}}\ , \tag{29}$$

where

$$\underline{D}=\int\varphi^{(n)\dagger}\varphi^{(k)}d\tau\ , \tag{30}$$

$$q_s=(x^2-\tfrac{1}{3}r^2),\quad s=xx$$
$$=xz,\quad s=xz\ . \tag{31}$$

Equation (28) is used to account for the nonorthogonality of the two sets of spin orbitals in the initial- and final-state wave functions. Since the radial functions corresponding to a given spin orbital are determined independently for αLS, for every two terms considered we obtain two sets of spin orbitals $\varphi^{(n)}$, $\varphi^{(k)}$ which have no single orthogonality relationship between each other. The overlap then between orbitals φ_i and φ_j' associated with states αLS and $\alpha' L'S'$ is

$$\int\varphi_i^*(x)\varphi_j'(x)\,dx=\int_0^\infty dr\,r^2R_{l_i}(r)R'_{l'_j}(r)\times\delta_{l_i l'_j}\,\delta_{m_{l_i}m'_{l_j}}\,\delta_{m_{s_i}m'_{s_i}}\ . \tag{32}$$

We explicitly took this "nonorthogonality" problem into account by rigorously evaluating the N-electron integral of Eq. (28). The technique used was developed by Westhaus and Sinanoğlu,[3] who applied a method put forth by King, Stanton, Kim, Wyatt, and Parr.[39,40] Thus the "frozen core approximation"[41] is replaced by an exact evaluation of N-body integrals.

All the computations were carried out on the Yale IBM 7094/7040 DCS computer in which the wave functions obtained as described in Refs. 1 and 2 formed the input data.

Four types of wave functions [HF alone, HF plus internal correlation, HF plus semi-internal and orbital polarization correlations, and HF plus all nondynamical correlations, i.e., Eq. (12)] were considered in each of the two states in all possible combinations to compute a series of N-electron matrix elements. In this way, the explicit effects of the different types of correlations on the matrix elements can be observed. For the particular transitions considered, the effect of spin-orbit interaction is unimportant and was neglected.[42]

IV. RESULTS AND DISCUSSION

A. O I $^1S_0$-$^1D_2$ Line

Our results on the O I $^1S_0$-$^1D_2$ line are shown in Table I. The results of Garstang are also shown for comparison. The table exhibits the changes in the transition probability as the various types of nondynamical correlations are introduced into the wave functions of the upper and lower terms.

The value we obtain by using just the analytic HF wave functions of Roothaan and Kelly[43] is $A=1.422\ \mathrm{sec}^{-1}$. This value is in disagreement with Garstang's value of $A=1.28\ \mathrm{sec}^{-1}$ obtained using the numerical HF wave functions of Hartree *et al.*[27] The difference could be due to Garstang's evaluation of the quadrupole integral s_q, with the radial function $R(2p)$ of the ground state $3P$ of oxygen instead of the two functions $R(2p)$ of ^1S and $R'(2p)$ of ^1D. The $R(2p)$ ^3P function, being less diffuse, has apparently given a smaller value than the "true" HF $s_q(^1S$-$^1D)$. He has obtained $s_q=0.790$. From our N-body calculation we obtain directly the HF line strength S_Q. Dividing by the angular factor $(\frac{20}{3})$ [see Eq. (2)] characteristic of the $^1S_0$-$^1D_2$ line we can obtain an "effective" quadrupole integral $s_q^{\mathrm{eff(HF)}}$ which includes the overlap of the two sets of orbitals. That is

$$s_q^{\mathrm{eff\,(HF)}}=[S_Q^{(\mathrm{HF})}/F_Q(LSJ,L'SJ')]^{1/2}\ , \tag{33}$$

where $S_Q^{(\mathrm{HF})}$ is the N-electron (includes overlap) HF result and $F_Q(LSJ, L'SJ')$ is defined in Eq. (2). We find $s_q^{\mathrm{eff(HF)}}=0.827$ while a straightforward calculation of the s_q integral using the $2p$ orbitals

TABLE I. Comparison of the calculated O I $^1S_0$-$^1D_2$ electric quadrupole transition probabilities (in sec^{-1}) with the different correlation effects taken explicitly into account in either the ground or the excited state or in both.

$^1S_0$ \ $^1D_2$	Present work[a]				Garstang (Ref. 6)	
	ϕ_{RHF}	$\phi_{\mathrm{RHF}}+\chi_{\mathrm{int}}$	$\phi+\chi_F$	Ψ_{CD}[b]	HF	HF + $2p^6\,{}^1S$
ϕ_{RHF}	1.422	1.368	1.425	1.345	1.28	1.25
Ψ_{CD}[b]	1.250	1.205	1.253	1.183		

[a] Using the new theory of atomic structure including electron correlation in ground and excited states (Ref. 1).

[b] Equation (12).

TABLE II. Theoretical electric quadrupole transition probabilities A_Q (in sec^{-1}), quadrupole line strengths S_Q (in a.u.), and "effective" (cf. text) quadrupole integral s_q^{eff} (in a.u.). The wave functions Ψ_{CD} include all the nondynamical correlation effects [Eq. (12) in text]. Results from the use of just restricted HF wave functions are also reported for comparison.

	Present work[a]					N.B.S. (Ref. 48)		
	A_Q		S_Q		$s_q$eff[b]			
Transitions	ϕ_{RHF}	Ψ_{CD}	ϕ_{RHF}	Ψ_{CD}	ϕ_{RHF}	A_Q	S_Q	s_q
O I $^1D_2$-$^1S_0$	1.422	1.183	4.567	3.801	0.827	1.34[c]	4.31	0.790[d]
O II $^2D_{5/2}$-$^2P_{3/2}$	0.1060	0.0915	5.3039	4.5809	0.615	0.106	5.30	0.616[e]
$^2D_{5/2}$-$^2P_{1/2}$	0.0606	0.0523	1.5154	1.3088		0.0610	1.52	
$^2D_{3/2}$-$^2P_{3/2}$	0.0449	0.0388	2.2731	1.9632		0.0450	2.29	
$^2D_{3/2}$-$^2P_{1/2}$	0.0902	0.0799	2.2731	1.9632		0.0900	2.27	
O III $^1D_2$-$^1S_0$	1.824	1.654	1.717	1.557	0.507	1.60	1.51	0.479[d]
N I $^2D_{5/2}$-$^2P_{3/2}$	0.0590	0.0489	17.0819	14.1545	1.104	0.054	15.6	1.027[f]
$^1D_{5/2}$-$^2P_{1/2}$	0.0337	0.0279	4.8805	4.0441		0.0308	4.45	
$^2D_{3/2}$-$^2P_{3/2}$	0.0251	0.0208	7.3208	6.0662		0.0230	6.7	
$^2D_{3/2}$-$^2P_{1/2}$	0.0504	0.0417	7.3208	6.0662		0.0460	6.7	
N II $^1D_2$-$^1S_0$	1.240	1.082	4.661	4.065	0.836	1.08	4.06	0.785[d]
C I $^1D_2$-$^1S_0$	0.650	0.548	19.61	16.473	1.715	0.50	15.1	1.51[d]

[a] Using the new theory of atomic structure including electron correlation in ground and excited states (Ref. 1).

[b] Equation (33) in text.

[c] This is an average of the theoretical value by Garstang (Ref. 6) and the experimental one by Omholt (Ref. 17).

[d] Reference 21.

[e] Reference 31.

[f] Reference 29.

of the ^1S and ^1D states given in Ref. (43) gives $s_q = 0.826$, a very small difference, which shows that overlap is practically unity. As discussed below in connection with other transitions, calculations by Seaton and Osterbrock[31] and by Froese[44] of quadrupole integrals using numerical HF wave functions are in agreement with our HF results while Garstang's values are consistently smaller.

The inclusion of only the internal part for the $^1S_0$ state gave a result of $A = 1.368$ sec^{-1}. This is a reduction of about 4% over the HF value, a result similar to that of Garstang[6] in his study on the effect of a limited configuration-interaction on electric quadrupole transition probabilities.

A further examination of Table I reveals that the semi-internal and polarization corrections in the $^1S_0$ term contribute little. The largest effect by far comes from the internal correlations. Indeed, it is likely that the N-body integrals over the quadrupole operator itself, which involves χ_F for the $^1S_0$ term, nearly vanish due to orbital orthogonality. The chief, though small, contribution of this χ_F is probably reflected in a normalization correction. We must not conclude, however, that the dominance of the internal correlation effects in the $^1S_0$ negates the importance of the semi-internal effects in other states. For whenever the internal effects are excluded by symmetry considerations, the semi-internal correlations assume a dominant and presumably significant role. The transition at hand is a case in point. No internal correlations are found in the $^1D_2$ term because of symmetry restrictions. Thus, the entire nondynamical correlations are found in the χ_F, which indeed reduces A substantially from 1.345 sec^{-1} to 1.183 sec^{-1}.

This last result of $A(5577) = 1.183$ sec^{-1}, obtained by using very detailed and accurate N-electron wave functions, is our value for the transition probability of the O I $^1S_0$-$^1D_2$ line.

As mentioned before, a sufficiently accurate experimental result which could be compared with our theoretical result does not exist. It should be noted that an apparent agreement with "experiment" could be obtained if Omholt's data were given a different interpretation.[17] From his graph in Ref. 17 there are a number of observed lifetimes greater than his quoted upper limit. Exactly why the limit of $\tau = 0.75$ sec is set is not clear, but it appears from the data that a slightly larger radiative lifetime (≈ 0.80 sec) of the $^1S_0$ state is not unreasonable. Combining this with the transition probability $A(2972) = 0.067$ sec^{-1} of the $^1S_0$-$^3P_1$ magnetic dipole line,[20,45] one can obtain a value of $A(5577) \approx 1.20$ sec^{-1} quite close to our result. Of course, this apparent agreement of theory with experiment must be considered with caution because of the uncertainty in the interpretation of the experimental data.

The absolute measurement of the transition probability made in the laboratory[15] is, as we discussed, uncertain by a factor of 2. The largest contribution to this uncertainty (50%) comes from the oscillator-strength value of the allowed ^1S-^1P transition (calculated from HF wave functions). For, as our results on allowed transitions using the present theory[3,5a,34] show, inclusion of electron correlation may alter the HF results by as much as a factor of 3. Since the experimentally derived transition probability $A(5577)$ is proportional to the ^1S-^1P oscillator strength, a meaningful comparison of this experiment with our result cannot be made until an accurate value for the ^1S-^1P oscillator strength is known.

As discussed in Sec. II and in Ref. 46, the ratio of $A(5577)/A(2972)$ has been experimentally found to be[14] 22 ± 2 and[16] 18.6 ± 3.7. Considering the accuracy of our present result on $A(5577) = 1.183$ sec^{-1} to be $\pm 3\%$ and also estimating an error of 5% for the $^1S_0$-$^3P_1$ magnetic dipole transition probability $A(2972) = 0.067$ sec^{-1} from Ref. 20, we propose a theoretical ratio of $A(5577)/A(2972) = 17.6 \pm 1.4$ fairly close to the experimental ratio of Ref. 16.

B. C I ^1S-^1D, N I ^2P-^2D, N II ^1S-^1D, O II ^2P-^2D, O III ^1S-^1D Lines

As in O I, the calculated transition probabilities for the O II, O III, N I, N II, C I ions clearly show the influence of the different electron correlation effects on the electric quadrupole transition probabilities. The HF values are the largest while inclusion of all nondynamical correlations result in smaller values. In Table II, we have listed the transition probabilities A_Q (in sec^{-1}) and the line strengths S_Q (in a.u.) calculated from the RHF wave functions and from the nondynamical [i.e., Ψ_{CD} of Eq. (12)] wave functions. We also give our values of the "effective" HF quadrupole integral $s_q^{\text{eff(HF)}}$ which includes the overlap of the two sets of HF spin orbitals as obtained in our N-body calculations (Eq. 33). However, we have calculated this overlap to be very close to unity so that $s_q^{\text{eff(HF)}} \approx s_q$. The N.B.S. accepted values,[47] based upon previous HF calculations—O I, O III, N I, N II, C I by Garstang[6,21] and O II by Seaton and Osterbrock[31]—are also given for comparison. Our HF results give a consistently larger value than those of Garstang's. However, the HF values of Seaton and Osterbrock[31] for the O II ^2P-^2D case agree very well with ours. Also, Froese[44] in recent calculations with accurate numerical HF wave functions, has obtained values of the quadrupole integrals of the $^1S_0$-$^1D_2$ transitions in C I, N II, and O III. Her values are: s_q (O III $^1S_0$-$^1D_2$) = 0.508, s_q (N II $^1S_0$-$^1D_2$) = 0.837, and s_q (C I $^1S_0$-$^1D_2$) = 1.715, which are in excellent agreement with ours: $s_q^{\text{eff(HF)}}$ (O III $^1S_0$-$^1D_2$) = 0.507, $s_q^{\text{eff(HF)}}$ (N II $^1S_0$-$^1D_2$) = 0.836, and $s_q^{\text{eff(HF)}}$ (C I $^1S_0$-$^1D_2$) = 1.715. It is also interesting to note that a similar agreement between results on s_q from analytical (Roothaan type) and numerical (Froese) HF wave functions has been reported by Steele and Trefftz[48] for several transitions in the F XIV ion. It is then apparent that the results of Garstang are not the "true" HF results for the transitions of interest, possibly because of his use of ground-state wave functions instead of the actual wave functions of the states involved in the transitions. Here we should mention that the

TABLE III. Variation of electric quadrupole transition probabilities with improving wave functions. Our results, using detailed correlated many-electron functions, must be accurate to within 5% (cf. text).

Transition	Screened hydrogenic (Ref. 19)	Hartree	Analytical variational	Hartree-Fock	Hartree-Fock plus electron correlation[a]
O I $^1S_0$-$^1D_2$	2.2	2.0[b]		1.28[c]	
		2.04[d]		1.422[a]	1.183
O II $^2D_{5/2}$-$^2P_{3/2}$	0.23	0.237[d]		0.106[e]	
				0.106[a]	0.0915
O III $^1S_0$-$^1D_2$	2.8	1.8[b]	2.00[f]	1.60[d]	
		1.805[d]		1.825[g]	
				1.824[a]	1.654
N I $^2D_{5/2}$-$^2P_{3/2}$	0.16			0.054[h]	
				0.0590[a]	0.0489
N II $^1S_0$-$^1D_2$	2.2	1.7[d]	1.822[d]	1.08[f]	
			1.350[f]	1.240[g]	
				1.240[a]	1.082
C I $^1S_0$-$^1D_2$	1.4	1.0[b]	0.849[d]	0.50[f]	
			0.62[f]	0.650[g]	
				0.650[a]	0.542

[a] Present work (based on Ref. 1).
[b] Reference 18.
[c] Reference 21.
[d] Reference 20.
[e] Reference 31.
[f] Reference 30.
[g] Reference 44.
[h] Reference 29.

Hartree, Hartree, and Swirles[27] wave functions are not too accurate for large r.[49]

Finally, in Table III we compare all the available theoretical electric quadrupole transition probabilities for [C], [N], and [O]. We can observe that the effect of exchange from Hartree to HF on these lines is quite important. The screened hydrogenic and various analytical wave functions are not reliable.

When all the nondynamical correlation effects [Ψ_{CD}, Eq. (12)] are taken into account, the main concern of the present paper, the values obtained are smaller by 13–17% than the HF ones. A similar reduction of the HF results of electric quadrupole transition probabilities in other atoms or ions of the first row should be expected when electron correlation is considered.

V. CONCLUSION

This paper presented a new method for the prediction of $E2$ transition probabilities which differs from the conventional central-field methods in the detailed inclusion of electron correlation effects in both of the states and of different central fields and many-electron matrix elements.

Having taken the effects of electron correlation as shown by the NCMET of atoms (see I) into account, detailed calculations of some important electric quadrupole transition probabilities have been made. A systematic examination of the effect of correlation on the transition probabilities of the electric quadrupole lines was considered. Our results indicate with certainty an improvement over the HF values in reducing them by 13–17%, which may be a typical order of magnitude of the effect on other electric quadrupole lines as compared to HF results. In view of the accuracy of the extensive wave functions used and of the method of calculation, we expect are values to be accurate with less than 5% uncertainty. In particular, in the case of the important O I $^1S_0$-$^1D_2$ transition, the previously accepted average transition probability[47] of $A_Q = 1.34\ \mathrm{sec}^{-1}$ is significantly reduced to $A_Q = 1.183\ \mathrm{sec}^{-1}$, the new value given by this work. The new theoretical values, based on the detailed atomic-structure theory, should be useful in atmospheric and astrophysical applications. It is hoped that new experimental methods for the measurement of these forbidden-transition probabilities will be developed.

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$$\langle \hat{F}_i \mid \hat{F}_j \rangle = D_{ii}\delta_{ij}.$$

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Correlation Energy of the Neon Atom*

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The linked-cluster many-body perturbation theory has been applied in a calculation of the correlation energy of the neon atom in the ground state (${}^1S$). The pair-correlation energy, obtained by summing the correlation energy between all pairs of states in the atom, is found to be −0.413 26 a.u. About 5% of the pair-correlation energy comes from excitations to *g*, *h*, and *i* states. Pair-pair interactions are found to be important and contribute 0.022 44 a.u. to the correlation energy. Correlation diagrams involving simultaneous excitations of three and more particles are found to be relatively unimportant and lead to a net contribution of only about 0.003 a.u. Our final value for the correlation energy is −0.389 14 a.u., which is in excellent agreement with the nonrelativistic experimental correlation energy of −0.389 a.u. A detailed comparison is made with the available configuration interaction calculations both with respect to numerical results as well as to the relative importance of various physical effects which contribute to the correlation energy.

I. INTRODUCTION

The study of many-body effects in atomic systems is currently in an accelerated state of development judging by the increasing number of publications in this field and the variety of atomic properties for which many-body effects are being analyzed. The procedures in most frequent use at the present time can be classified broadly under two categories: variational and perturbation types. All the current variational approaches for atoms with more than two or three electrons use the con-