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Theory of Atomic Structure Including Electron Correlation. I. Three Kinds of Correlation in Ground and Excited Configurations

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There are novel correlation effects in excited states and configurations unlike those in closed shells. A theory for general nonclosed shells, and a method for calculation, are developed by separating the correlations into three mathematically and physically distinct types: (1) "internal," (2) "polarization plus semi-internal," and (3) "all-external" correlations. The first two of these are unique to open shells and strongly dependent on number of electrons, symmetry, and Z. They are however shown to be calculable by a finite configuration interaction method, and their energy contributions and wave functions are computed using a fully automatic program for 113 states of $1s^22s^n2p^m$ ($n = 0, 1, 2$; $m = 0, 1, \dots, 6$) configurations for $Z = 5$ through 11. Both effects are found to be important in magnitude. The detailed wave functions obtained, which include those of positive and negative ions and of highly excited states containing inner $2s$ holes, are useful for obtaining atomic properties such as transition probabilities. The remaining all-external correlation energy is found to be, as predicted by the present theory, just like the correlation in closed shells, i.e., mainly made up of transferable pair correlations (evaluated in Paper II) and approximately transferable through Z in a given isoelectronic sequence.

I. INTRODUCTION

It was shown some time ago by one of us[1,2] that the N-electron correlation problem for closed-shell atoms and molecules can by and large be reduced to $N(N-1)/2$ separate variational pair-correlation calculations. This was done first by using perturbation theory in closed form and with operator techniques taking the Hartree-Fock (HF) wave function as unperturbed.[2] In a later series of papers,[3-7] titled "Many Electron Theory of Atoms and Molecules" (MET), giving a nonperturbative treatment, the actual pair correlations were shown to be approximately decoupled by examining three and more electron correlations and the effects of correlation on orbitals. In the absence of vacant HF orbitals degenerate or nearly degenerate with occupied ones, the pairs were also quite insensitive to the number of electrons N, symmetry state, and to a lesser extent Z[6]. For example, the $1s$-$1s$ pair correlation could approximately be transferred from one ion to another or between symmetry states of a given ion. Pairs possessing this transferability property were called "dynamical."

The theory was extended to single-determinantal ground states of nonclosed-shell atoms by McKoy and Sinanoğlu.[7] Their treatment of the first row revealed certain nontransferable pair correlations. For example, the $2s$-$2s$ correlation energy, $\epsilon(2s^2)$, in ground states of $1s^2 2s^2 2p^n (n=0,1,\ldots,6)$, does not only increase with Z for an isoelectronic sequence[8] but also, for a given Z, falls off linearly in magnitude with the number of $2p$ electrons with parallel spin (e.g., from 3.2 eV in Ne^{+6} to 0.27 eV in neutral Ne).[7] Thus two types of pair correlations, dynamical (transferable) and nondynamical (nontransferable) were distinguished.

Further, and novel, correlation effects arise in general nonclosed shells, and in excited states and configurations. These cases were initially studied by perturbation theory.[9] The present nonperturbative theory was first outlined by Sinanoğlu[10] and preliminary calculations were carried out by Skutnik.[11,12] The general nonclosed-shell theory separates the total correlation into three physically and mathematically distinct types. Two of these, (1) the "internal" and (2) the "semi-internal" correlations, are unique to nonclosed shells and are not dynamical. They are specific to each Z, N, and symmetry state. The third type, (3) the "all-external" correlations, consists of dynamical pairs quite similar to those in closed shells. In the present paper the specific internal and semi-internal effects are calculated for 113 species arising from $1s^2 2s^n 2p^m (n=0,1,2;\ m=0,1,\ldots,6)$ configurations of B, C, N, O, F, Ne, and Na atoms and their ions. The all-external effect is then evaluated for each species by subtracting the specific effects from the total "experimental" correlation energy. The new semi-internal correlation energy effect as well as the internal are found to be of important magnitudes. The all-external correlation energy is seen to be approximately Z – transferable as predicted by MET. In subsequent papers of this series, the detailed wave functions obtained will be used to calculate atomic transition probabilities. The all-external correlation energies will be decomposed into a set of pair correlations applicable to excited as well as ground configurations. The combinations of these results will be used to predict transition energies, electron affinities, and negative-ion excited states. Detailed comparison with experiment, where available, will also be given.

II. CORRELATION IN CLOSED AND OPEN SHELLS

A. Closed Shells

The exact closed-shell wave function is written as

$$\Psi = \phi_0 + \chi \ , \tag{1}$$

where ϕ_0 and χ are, respectively, the HF and correlation functions. ϕ is made of an antisymmetrized product of N spin orbitals k:

$$\phi_0 = \mathcal{A}(1\,2\,3 \cdots k \cdots N) \tag{2}$$

and the following orthogonality and normalization conventions hold

$$\langle \phi_0 | \chi \rangle = 0; \ \langle \phi_0 | \phi_0 \rangle = 1, \quad \text{hence } \langle \phi_0 | \Psi \rangle = 1 \, . \tag{3}$$

χ is analyzed into $1,2,3,\ldots,N$ particle correlation parts by the "method of successive partial orthogonalizations."[13] The detailed form of χ one gets from this analysis is

$$\chi = \sum_{i \geq 1}^{N} \{\hat{f}_i\} + \sum_{i>j}^{N} \{\hat{U}'_{ij}\} + \sum_{i>j>l}^{N} \{\hat{U}'_{ijl}\} + \cdots + \{\hat{U}'_{12\cdots N}\} \, . \tag{4}$$

$\{\hat{f}_i\}, \{\hat{U}'_{ij}\}, \ldots, \{\hat{U}_{12\cdots N}\}$ are $1,2,\ldots,N$ electron correlation parts:

$$\{\hat{U}'_{ij\cdots n}\} = \frac{\mathcal{A}}{(n!)^{1/2}} \left((1\,2 \cdots N) \frac{\hat{u}'_{ij\cdots n}}{(ij\cdots n)} \right), \tag{5}$$

where the symbolic division by $(ij\cdots n)$ indicates the absence of these orbitals from the HF product $(12\cdots N)$. The n-electron correlation functions have the following orthogonality and antisymmetry properties:

$$\langle \hat{u}'_{ij\cdots n} | k \rangle_{\vec{x}_i} = \int \hat{u}'^{*}_{ij\cdots n}(\vec{x}_i, \vec{x}_j, \ldots, \vec{x}_n) k(\vec{x}_i) d\vec{x}_i = 0 \ , \tag{6}$$

$$\hat{u}'_{ij\cdots n}(\vec{x}_i, \vec{x}_j, \ldots, \vec{x}_n) = -\hat{u}'_{ij\cdots n}(\vec{x}_j, \vec{x}_i, \ldots, \vec{x}_n) \, .$$

(The $\vec{x}_i$ above refer to space *and* spin coordinates.)

The exact nonrelativistic energy is[14]

$$E = \langle \phi_0 | \mathcal{H} | \phi_0 \rangle + \langle \phi_0 | \mathcal{H} | \chi \rangle = E_{\mathrm{HF}} + E_{\mathrm{CORR}}, \quad (7)$$

where

$$E_{\mathrm{HF}} = \langle \phi_0 | \mathcal{H} | \phi_0 \rangle; \quad E_{\mathrm{CORR}} = \langle \phi_0 | \mathcal{H} | \chi \rangle. \quad (8)$$

All equations given up to this point are exact. But they only amount to a re-expression of the Schrödinger equation. However, further analysis by MET yields the following simplifications[3-5]:

(a) Owing to the properties of the HF orbital, short range of the "fluctuation potential"[3] and antisymmetry, only pair correlations, $\hat{u}'_{ij}$, are important. One- and odd-particle correlations are small, and even-electron correlations are to a good approximation given by a sum of "unlinked products" of $\hat{u}'_{ij}$, e.g.,

$$\hat{u}'_{ijkl} \simeq \hat{u}_{ijkl} = \tfrac{1}{2}\,\mathfrak{A}_4[\hat{u}_{ij}\hat{u}_{kl} + \hat{u}_{ik}\hat{u}_{jl} + \hat{u}_{il}\hat{u}_{jk}]\,. \quad (9)$$

$\mathfrak{A}_4$ is the four-electron antisymmetrizer. The prime on $\hat{u}$ indicates inclusion of "linked clusters." (Note that "linked" and "unlinked" are terms used here as defined and used in MET.[3] They have entirely different meanings than the similar words used in diagrammatic perturbation theory.)

(b) For the same reasons, pair correlations are decoupled and approximately transferable. The correlation function now becomes

$$\chi \simeq \chi'_s = \mathfrak{A}\left[(1\,2\,3\cdots N)\left(2^{-1/2}\sum_{i>j}^{N}\frac{\hat{u}_{ij}}{(ij)} + \frac{1}{2}\sum_{\substack{i>j\\ i,j\neq k,l}}^{N}\sum_{k>l}^{N}\frac{\hat{u}_{ij}\hat{u}_{kl}}{(ijkl)} + \frac{1}{2(2)^{1/2}}\sum_{\substack{i>j\\ i,j\neq k,l\neq m,n}}^{N}\sum_{k>l}^{N}\sum_{m>n}^{N}\frac{\hat{u}_{ij}\hat{u}_{kl}\hat{u}_{mn}}{(ijklmn)} + \cdots\right)\right], \quad (10)$$

and the energy is again given by[15]

$$E \simeq \langle \phi_0 | \mathcal{H} | \phi_0 \rangle + \langle \phi_0 | \mathcal{H} | \chi'_s \rangle = E_{\mathrm{HF}} + E_{\mathrm{CORR}}\,. \quad (11)$$

But the $\hat{u}_{kj}$ are now separately calculable.

A graphical exposition of these ideas is given in Fig. 1. The shaded circle A represents the filled HF sea,[16] and the outside region B is χ. Electrons originally in orbitals i and j correlate and make virtual transitions to a pair-correlation function $\hat{u}_{ij}$ outside[17] the HF sea.

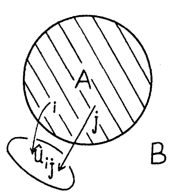

FIG. 1. Pair correlations in closed shells. A pair of electrons, originally in orbitals i and j in the HF sea A, correlate and go to a pair correlation function $\hat{u}_{ij}$ outside the sea (in B).

B. Nonclosed Shells

In nonclosed shells, some of the orbitals in A are unoccupied. The vacancies in the HF sea cause novel correlation effects which do not exist in closed shells. These are illustrated in Fig. 2(a)–2(c). In 2(a), electrons in k and k' correlate but shift to unoccupied orbitals in A and remain in the sea. In 2(b), one electron shifts within the sea to an unoccupied orbital 1, while the other goes out to a one-electron correlation function $\hat{f}$. Finally in 2(c) a pair excitation analogous to those in closed shells occurs, and electrons in k and k' end up in a pair-correlation function $\hat{u}_{kk'}$. These three effects are, respectively, the "internal," the "semi-internal," and the "all-external" correlations. The decoupling and transferability

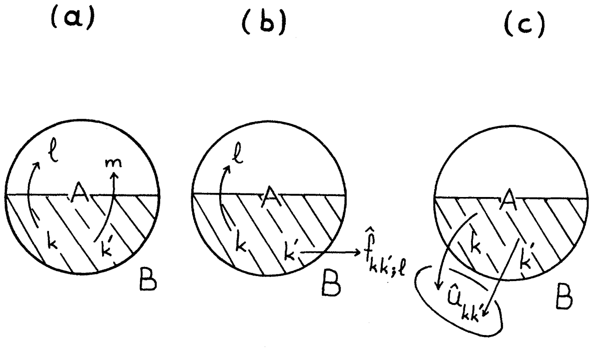

FIG. 2. The three kinds of correlation in nonclosed shell systems. For first-row atoms all 1s, 2s, 2p spin orbitals (occupied and vacant) constitute the Hartree-Fock sea (RHF), denoted by A. (a) An "internal" correlation effect. Electrons shift from occupied to vacant Hartree-Fock orbitals. (b) A "semi-internal" correlation effect. An electron shifts within the partly filled RHF sea, while the other goes to a function in B. (c) An "all-external" pair correlation. Both electrons are ejected out of the HF sea into a pair correlation $\hat{u}_{kk'}$ in B similar to those in the closed shell MET.

properties still hold for the all-external pairs. But the internal and semi-internal correlations involve vacant orbitals lying close to the occupied ones and are quite sensitive to N, symmetry, and Z.

For general nonclosed-shell states there are several self-consistent-field (SCF) procedures. Among these both the multiconfigurational or generalized restricted HF (GRHF)[18-20] or Roothaan's single configurational restricted HF (RHF)[21-24] are suitable starting points.[9] However, RHF calculations are more easily available in literature, and for this reason they are preferred in the present calculation. The correspondence between RHF and GRHF starting points are straightforward both in formalism and calculation.

If the HF sea has M orbitals and the species under consideration has N electrons,

$$\binom{M}{M} = \frac{M!}{N!\,(M-N)!}\,,$$

different antisymmetrized products (Slater determinants) are possible. The GRHF wave function is in general a linear combination of these determinants:

$$\phi_{\mathrm{GRHF}} = \sum_{K\geqslant 1}^{\binom{M}{N}} C_K \Delta_K\,, \qquad (12)$$

$$\Delta_K = \mathfrak{a}(k_1(\vec{x}_1)k_2(\vec{x}_2)\cdots k_N(\vec{x}_n))\,,$$

where $\{k_i\}$ is a set of N orbitals out of M, and $\vec{x}_i$ represents space and spin coordinates of particle i. Many of the C_K may be zero because of symmetry.

While ϕ_{GRHF} contains determinants of all possible configurations within the sea, ϕ_{RHF} is restricted to the single main configuration. For the ground configuration of $N=6$, for example, ϕ_{RHF} contains only determinants of $1s^2 2s^2 2p^2$ type while ϕ_{GRHF} has $1s^2 2p^4$, $1s2s2p^4$, $2s^2 2p^4$, and $2p^6$ as well (others are forbidden by parity). The wave function with correlation for GRHF is

$$\Psi = \phi_{\mathrm{GRHF}} + \chi\,, \qquad (13)$$

with

$$\langle \phi_{\mathrm{GRHF}} | \chi \rangle = 0 \quad \text{and} \quad \langle \phi_{\mathrm{GRHF}} | \phi_{\mathrm{GRHF}} \rangle = 1\,,$$

while for RHF

$$\Psi = \phi_{\mathrm{RHF}} + \chi_{\mathrm{int}} + \chi_{\mathrm{ext}}$$

with

$$\langle \phi_{\mathrm{RHF}} | \chi_{\mathrm{int}} \rangle = \langle \phi_{\mathrm{RHF}} | \chi_{\mathrm{ext}} \rangle = \langle \chi_{\mathrm{int}} | \chi_{\mathrm{ext}} \rangle = 0\,,$$

and

$$\langle \phi_{\mathrm{RHF}} | \phi_{\mathrm{RHF}} \rangle = 1\,. \qquad (14)$$

The internal correlation function χ_{int} of Eq. (14) contains all virtual transitions that shift the electrons within the HF sea. This part is included in ϕ_{GRHF} and made self-consistent with the basic configuration while RHF treats it as a correlation effect. Thus

$$\phi_{\mathrm{GRHF}} \simeq \frac{\phi_{\mathrm{RHF}} + \chi_{\mathrm{int}}}{(1 + \langle \chi_{\mathrm{int}} | \chi_{\mathrm{int}} \rangle)^{1/2}}\,. \qquad (15)$$

The difference between the two sides of this equation amounts to the effect of internal correlation χ_{int} on ϕ_{RHF} orbitals and is quite small[5] as our calculations show (Table I).

The detailed wave function with GRHF in the unlinked cluster approximation is[9]

$$\phi_{\mathrm{GRHF}} + \chi_d' = \sum_{K\geqslant 1}^{\binom{M}{N}} C_K(\Delta_K + \chi_K')\,, \qquad (16)$$

$$\chi_K' = \mathfrak{a}\Bigg[(k_1k_2\cdots k_N)\Bigg(\sum_{a\geqslant 1}^{N} \frac{\hat{f}_{k_a}^{K}}{(k_a)} + \sum_{a>b}^{N} \sum_{\substack{l\geqslant 1 \\ l\neq k_1,k_2,\ldots,k_N}}^{M} \frac{l\hat{f}^{K}_{k_ak_b;l}}{(k_ak_b)} + 2^{-1/2}\sum_{a>b}^{N} \frac{\hat{u}^{K}_{k_ak_b}}{(k_ak_b)} + \{\text{unlinked clusters}\}\Bigg)\Bigg]\,.$$

There is a correlation function χ_k' for every GRHF determinant Δ_K. Each χ_K' contains:

(a) Single-electron excitations $\hat{f}_k^{K}$ arising from orbital average polarizations or spin and symmetry polarizations. Single excitations which have the same symmetry as the orbital they replace are similar to single excitations in closed shells and are expected to be small.[5] They do not appear in the first-order perturbation wave function.[13] Spin and symmetry polarizations are unique to open shells and are due to the nonspherical character of open-shell HF potential.

(b) Two-electron transitions where electrons originally in k and k' correlate and one goes to spin orbital l, which is in the HF sea but not in Δ_K, while the other ends up in a one-electron correlation function $\hat{f}^{K}_{kk';l}$ outside the sea. This is the semi-internal correlation effect, unique to open shells and corresponds to the process of Fig. 2(b); $kk' \to l\hat{f}_{kk';l}$

(c) Virtual pair excitations $\hat{u}_{kk'}$ from orbitals

TABLE I. Comparison of internal correlation energies E_{int} (in eV). Here PC gives the present calculation [these values are from separate internal CI (see text, Sec. IIIC, also cf. Table III]; MS gives the values of McKoy and Sinanoğlu (Ref. 7); and TCSCF gives the values from the two-configurational SCF (Ref. 20).

		$Z=6$			$Z=8$			$Z=10$	
Species	PC	MC	TCSCF	PC	MC	TCSCF	PC	MC	TCSCF
$1s^2 2s^2 2p\ {}^2P$	−1.101	−1.069	−1.110	−1.529	−1.477	−1.543	−1.923	−1.882	−1.941
${}^3P$	−0.468	−0.457	−0.472	−0.682	−0.656	−0.686	−0.864	−0.832	−0.869
$1s^2 2s^2 2p^2\ {}^1D$	−0.452	⋯	⋯	−0.679	⋯	⋯	−0.863	⋯	⋯
${}^1S$	−1.594	⋯	⋯	−2.540	⋯	⋯	−3.282	⋯	⋯
$1s^2 2s^2 2p^3\ {}^2P$	−0.602	⋯	⋯	−1.155	⋯	−1.153	−1.510	⋯	−1.520
$1s^2 2s^2 2p^4\ {}^1S$	⋯	⋯	⋯	−1.443	⋯	−1.457	−1.991	⋯	−2.006

k and k' of Δ_k [Fig. 2(c)]. This process is similar to pair correlations in closed shells.

All these correlation functions are one-electron orthogonal to HF sea orbitals:

$$\langle \hat{f}_k{}^K | i \rangle_{\vec{x}_i} = \langle \hat{f}^K_{kk';l} | i \rangle_{\vec{x}_i} = \langle \hat{u}_{kk'} | i \rangle_{\vec{x}_i} = 0 , \qquad (17)$$

and the antisymmetry of $\hat{u}_{kk'}{}^K$ still holds (Eq. 6). {Unlinked clusters} contain products of a, b, and c type correlations. Unlinked clusters with more than one $\hat{f}_k{}^K$ or $\hat{f}_{kk'}{}^K$ are neglected.[9,10]

To make the transition to RHF we write Eq. (16) as

$$\phi_{\text{GRHF}} + \chi_d' = \sum_{K \geq 1}^{\kappa} C_K (\Delta_K + \chi_K') + \sum_{K > \kappa}^{\binom{M}{N}} C_K (\Delta_K + \chi_K') . \qquad (18)$$

Determinants 1 to κ belong to the basic configuration, and $\kappa + 1$ to $\binom{M}{N}$ to the rest. Now if we restrict self-consistency to the first κ determinants and neglect the correlations coming from nonbasic configurations, Eq. (18) becomes

$$\Psi \simeq \phi_{\text{RHF}} + \sum_{K > \kappa}^{\binom{M}{N}} C_K \Delta_K + \sum_{K \geq 1}^{\kappa} C_K \chi_K' . \qquad (19)$$

Restriction of self-consistency to the basic configuration is equivalent to the approximation of Eq. (15). The χ_K' arising from nonbasic configurations are corrections to the internal correlation and are expected to be small. Rearranging the last summation we get

$$\Psi \simeq \phi_{\text{RHF}} + \chi_{\text{int}} + \chi_F + \chi_U , \qquad (20a)$$

where
$$\chi_{\text{int}} = \sum_{K > \kappa}^{\binom{M}{N}} C_K \Delta_K , \qquad (20b)$$

$$\chi_F = \sum_{K \geq 1}^{\kappa} C_K \left[\mathfrak{A}(k_c k_d \cdots k_N) \left(\sum_{a \geq 1}^{N} \frac{\hat{f}_{k_a}{}^K}{(k_a)} + \sum_{a > b}^{N} \sum_{\substack{l \geq 1 \\ l \neq k_c, k_d, \ldots, k_N}}^{M} \frac{l\hat{f}^K_{k_a k_b ; l}}{(k_a k_b)} \right) \right] , \qquad (20c)$$

$$\chi_U = \sum_{K \geq 1}^{\kappa} C_K \left[\mathfrak{A}(k_c k_d \cdots k_N) \times \left(2^{-1/2} \sum_{a > b} \frac{\hat{u}_{k_a} \hat{u}_{k_b}}{(k_a k_b)} + \{\text{unlinked clusters}\} \right) \right] . \qquad (20d)$$

The energy is[15]

$$E \simeq \langle \phi_{\text{RHF}} | \mathcal{H} | \phi_{\text{RHF}} \rangle + \langle \phi_{\text{RHF}} | \mathcal{H} | \chi_{\text{int}} \rangle + \langle \phi_{\text{RHF}} | \mathcal{H} | \chi_F \rangle + \langle \phi_{\text{RHF}} | \mathcal{H} | \chi_U \rangle ,$$

i.e.,
$$E \simeq E_{\text{RHF}} + E_{\text{int}} + E_F + E_U , \qquad (21)$$

respectively. The internal, χ_{int} and E_{int} [Fig. 2(a)], the polarization plus semi-internal, χ_F and E_F [Fig. 2(b)], and the all-external, χ_u and E_u [Fig. 2(c)], correlations are the three distinct correlation effects in nonclosed shells. The first two are specific, nontransferable effects unique to open shells. However, they can be calculated by a finite configuration interaction (CI). The all-external effect is similar to correlations in closed shells and gives a slowly convergent CI. But it is mainly made of transferable pair correlations and can be treated by semiempirical "pair-aufbau" techniques[6] (Paper II).

III. CALCULATION OF THE SPECIFIC CORRELATION EFFECTS

Equations (19)–(21) with the anonymous parentage approximation[9,25] provide the basis for our calculations. Both χ_{int} and χ_F are calculated by CI. An automatic CI program[26] for IBM 7040/7094 DCS was prepared and used to calculate χ_{int}, E_{int}, χ_F, and E_F for 113 species of B, C, N, O, F, Ne, and Na arising from $1s^2 2s^n 2p^m$ ($n=0,1,2$; $m=0,1,\ldots,6$) configurations.

In a CI calculation, one usually finds the correct symmetry combination for each configuration and then constructs the energy matrix H. Although this procedure results in a smaller CI matrix, the group theory algebra for finding correct combinations is time consuming. We constructed H directly from single determinants except for the ϕ_{RHF} which is left as a fixed symmetry combination. When the set of determinants used is closed under L^2 and S^2 the two procedures are equivalent and the matrices are related by a unitary transformation. The time lost in diagonalizing the larger matrix in the computer is compensated in bypassing the algebra. Closing the set under L^2 and S^2 introduces triple or higher virtual excitations and closed-shell-type single excitations which do not mix directly with ϕ_0.[12] We did not include these in most of our calculations though they could be included quite easily. Our wave functions in general are therefore not rigorous eigenfunctions of L^2 and S^2. However, a set of test runs was carried out to check for the energy error introduced by these omissions. The difference with the exact L^2 and S^2 eigenfunctions and with the more approximate ones was always less than 0.005 eV.

A. Internal Correlation

χ contains at most $\binom{M}{N} - \kappa$ determinants [Eq. (20)]. Many of these, however, have $C_K = 0$ due to symmetry. Because of the large energy gap, virtual transitions between K and L shells do not make appreciable contributions to E_{int}. Configurations arising from single-electron shifts between s and p orbitals are forbidden by parity. Therefore in the first row the only important contribution to χ_{int} comes from $2s^2 \rightarrow 2p^2$ mixing (i.e., $1s^2 2s^2 2p^n \rightarrow 1s^2 2p^{n+2}$ CI); hence the internal pair excitations of Fig. 2(a). These considerations restrict χ_{int} to at most three determinants for the first row. The internal correlation was calculated and studied systematically by McKoy and Sinanoğlu[3] as the "nondynamical part of $2s$-$2s$ pair correlations" for ground configurations of first-row atoms. Especially, the dependence on the number of electrons and the magnitudes in relation to the remaining dynamical $2s$-$2s$ correlations were studied. Clementi and Veillard[20] have repeated some of these studies with two configurational SCF calculations.

In the present calculation vacant $2s$ and $2p$ orbitals of $1s^2 2s^2 2p^n$ ($n \geqslant 1$) configurations were taken to have the same radial part as their occupied counterparts. For $1s^2 2p^2$ we used the $2s$ orbital of $1s^2 2s^2$ after orthogonalizing it to $1s$ of $1s^2 2p^2$. Vacant $2p$ orbitals were again assigned the radial part of the occupied ones. According to our arguments above, $1s^2 2s 2p^n$ configurations have no appreciable χ_{int}.

Some of our results are compared with those of Refs. 7 and 20 in Table I. Our calculations confirm the previous conclusions of (a) Linderberg and Shull[8] that E_{int} increases in magnitude with Z, and (b) of McKoy and Sinanoğlu[7] that for single determinantal ground states of first-row atoms it decreases in magnitude with the number of $2p$ electrons with parallel spin. Two configurational SCF calculations of Ref. 20 should be a good approximation to GRHF. The close agreement of the direct CI values of Ref. 7 and ours with those of Ref. 20 is an indication of the accuracy of the approximation in Eq. (15). Our extensive results are reported in Tables IV–VII. E_{int} values of Table I are results of CI between ϕ_{RHF} and internal-type virtual transitions χ_{int} only. E_{int} values of Tables IV–VII, on the other hand, are extracted[15] from CI between ϕ_{RHF} and $\chi_{\text{int}} + \chi_F$ and are therefore slightly different (see Sec. III C). Since the calculations of Refs. 7 and 20 involve only χ_{int}-type configurations, it is more reasonable to compare them with our $\phi_{\text{RHF}} \rightarrow \chi_{\text{int}}$ CI rather than $\phi_{\text{RHF}} \rightarrow (\chi_{\text{int}} + \chi_F)$.

B. Polarization and Semi-Internal Correlation

The χ_F yields a finite CI (in the sense below) because it is restricted to processes where only one electron is allowed to leave the HF sea. To see this consider χ_F in its CI expansion:

$$\chi_F = \textstyle\sum_i c_i{}^F \Delta_i{}^F \tag{22a}$$

and

$$E_F = \langle \phi_{\text{RHF}} | \mathcal{H} | \chi_F \rangle = \textstyle\sum_i c_i{}^F \langle \phi_{\text{RHF}} | \mathcal{H} | \Delta_i{}^F \rangle , \tag{22b}$$

where $\Delta_i{}^F$ are determinants containing $\hat{f}_k$ and $\hat{f}_{kk'}$ type virtual excitations. Let F signify a general χ_F-type excitation, $\hat{f}_k$ or $\hat{f}_{kk'}$. Consider any term $\langle \phi_{\text{RHF}} | \mathcal{H} | \Delta_i{}^F \rangle$ in the sum in (22b). In general it will contain one-electron integrals of the type $\langle k | h_i | F \rangle$ and two-electron integrals $\langle kk' | g | k'' F \rangle$, where h_i are the one-electron terms in the Hamiltonian and the k are HF sea orbitals. For the first row the k can be of s or p symmetry. Hence $\langle k | h_i | F \rangle = 0$ if F has d or higher symmetries. The bra in $\langle kk'|g|k''F\rangle$ can at most have $p\otimes p \rightarrow s$, p, d components. The ket $|kF\rangle$ cannot contain any of these if F has g or higher symmetries; if k is an s orbital then $s\otimes g \rightarrow g$, if it is p then $p\otimes g \rightarrow f$, g, h and none of these symmetries are present in $\langle kk'|$. Hence a Δ_i^F can mix[26] with ϕ_{RHF} only if F is s, p, d, or f. The CI for χ_F is therefore finite in the angular functions. The radial functions multiplying these can be well approximated by one radial term each, though if expanded in some radial basis set they would still be infinitely many.

The automatic program[26] was used to calculate χ_F and E_F. All F-type processes mixing[27] directly with ϕ_{RHF} were included. The determinants so selected are the dominant ones. The resulting full matrix is diagonalized. Assignment of radial part to virtual $2s$ and $2p$ orbitals for $1s^2 2s^2 2p^n$ and $1s^2 2p^2$ are the same as in χ_{int}. Virtual $2s$ and $2p$ orbitals of $1s^2 2s 2p^n$ were assigned the same radial parts as occupied ones.

Of course the symmetry arguments given above do not restrict the radial part of F as mentioned above which has to be varied to minimize the energy. These radial functions were approximated by single Slater-type orbitals [STO; $r^{n-1}\exp(-\alpha r)$] of $3s$, $3p$, $3d$, and $4f$ types. The energy has a very flat minimum with respect to variations of STO exponents. A variation of 0.1 (2–20%) around the optimum value usually affects the energy by less than 0.003 eV and always less than 0.01 eV. For this reason α_{3d} was varied in steps of 0.1 and $\alpha_{3s}=\alpha_{3p}=\alpha_{3d}$, and $(\alpha_{4f}/\alpha_{3d})=0.6$ was assumed. This ratio corresponds to maximum radial overlap between $r^2\exp(-\alpha_{3d}r)$ and $r^3\exp(-\alpha_{4f}r)$ $3s$ and $3p$ orbitals were kept radially orthogonal to RHF orbitals of the same symmetries.

Table II shows contributions of different kinds of χ_F-type processes to E_F for two examples.[15] In $1s^2 2s^2 2p^n$ configurations $\hat{f}_{2s2p';2p''}$-type excitations make the largest contribution. The greater part of the large $2s$-$2p$ interorbital correlation first noted by McKoy and Sinanoğlu[7] is due to this semi-internal effect. In $1s^2 2s 2p^n$ and $1s^2 2p^n$, $\hat{f}_{2p2p';2s}$-type contributions are as large or larger than $\hat{f}_{2s2p;2p'}$. Contributions of single excitations $\hat{f}_k$ are always smaller than those of semi-internal processes. Extensive results of our E_F calculations are reported in Tables IV–VII. E_F is seen to be of an important magnitude, comparable with and often larger than the internal correlation energy.

C. Additivity of the Three Types of Correlation Energy

For cases where both χ_{int} and χ_F were non-negligible, three separate CI calculations, one for $\phi_{\mathrm{RHF}} \rightarrow \chi_{\mathrm{int}}$ only, one for $\phi_{\mathrm{RHF}} \rightarrow \chi_F$ only, and one for $\phi_{\mathrm{RHF}} \rightarrow (\chi_{\mathrm{int}}+\chi_F)$ were carried out. The energy difference

$$E_{\mathrm{CI}}[\phi_{\mathrm{RHF}} \rightarrow (\chi_{\mathrm{int}}+\chi_F)] - [E_{\mathrm{CI}}(\phi_{\mathrm{RHF}} \rightarrow \chi_{\mathrm{int}}) + E_{\mathrm{CI}}(\phi_{\mathrm{RHF}} \rightarrow \chi_F)] \tag{23}$$

TABLE II. Energy contributions (in eV) of polarization and semi-internal correlations. Indices of $\hat{f}$ signify the sum of certain types of correlations, e.g.,

$$\hat{f}_{2s}=\hat{f}_{2s_\alpha}+\hat{f}_{2s_\beta},\ \hat{f}_{2s2s;\,2p}=\hat{f}_{2s_\alpha 2s_\beta;\,2p_{+\alpha}}+\hat{f}_{2s_\alpha 2s_\beta;\,2p_{-\beta}}+\cdots,\ \text{etc.}$$

The sum of the energy contributions is rigorously equal to E_F (Ref. 15 of text); apparent discrepancies are due to roundoff error.

$\hat{f}_{ij;\,l}$	$1s^2 2s^2 2p^4(^3D)$		$1s^2 2s^2 p^2(^2D)$		$1s^2 2p^2(^1D)$	
	$Z=8$	$Z=11$	$Z=6$	$Z=8$	$Z=7$	$Z=8$
$\hat{f}_{2s2s;\,2p}$	−0.002	−0.002	⋯	⋯	⋯	⋯
$\hat{f}_{2s2p;\,2s}$	⋯	⋯	−0.001	−0.000	⋯	⋯
$\hat{f}_{2s2p;\,2p}$	−0.973	−1.170	−0.599	−0.661	⋯	⋯
$\hat{f}_{2p2p;\,2s}$	⋯	⋯	−0.490	−0.448	−0.911	−0.871
$\hat{f}_{2p2p;\,2p}$	−0.037	−0.030	−0.027	−0.021	−0.012	−0.015
$\hat{f}_{2s}^{\,p}$	−0.019	−0.023	−0.001	0.000	⋯	⋯
$\hat{f}_{2p}^{\,p}$	−0.004	−0.003	−0.001	−0.001	−0.001	−0.001
E_F	−1.036	−1.227	−1.119	−1.132	−0.925	−0.887

TABLE III. Decoupling of $E_{\rm int}$ and E_F (in eV). The values of $E_{\rm int}(s)$, $E_F(s)$, and $E_{\rm int}(s)+E_F(s)$ are from separate CI (i,e., from $\phi_{\rm RHF} \leftrightarrow \chi_{\rm int}$ and $\phi_{\rm RHF} \leftrightarrow \chi_F$ separately; see text). The values of $E_{\rm int}(t)$, $E_F(t)$, and $E_{\rm int}(t)+E_F(t)$ are from total CI [i.e., $\phi_{\rm RHF} \leftrightarrow (\chi_{\rm int}+\chi_F)$ altogether; see text].

Species	Z	$E_{\rm int}(s)$	$E_{\rm int}(t)$	$E_F(s)$	$E_F(t)$	$E_{\rm int}(s)+E_F(s)$	$E_{\rm int}(t)+E_F(t)$
$1s^22s^22p(^2P)$	5	−0.827	−0.802	−0.613	−0.586	−1.440	−1.388
	6	−1.101	−1.088	−0.681	−0.662	−1.782	−1.750
	7	−1.323	−1.313	−0.728	−0.714	−2.051	−2.027
	8	−1.529	−1.522	−0.758	−0.747	−2.287	−2.269
	9	−1.728	−1.723	−0.779	−0.771	−2.507	−2.494
	10	−1.923	−1.920	−0.795	−0.789	−2.718	−2.709
	11	−2.117	−2.115	−0.807	−0.804	−2.924	−2.919
$1s^22s^22p^2(^1D)$	5	−0.205	−0.214	−0.783	−0.790	−0.988	−1.004
	6	−0.452	−0.438	−1.050	−1.032	−1.502	−1.470
	7	−0.576	−0.564	−1.169	−1.153	−1.745	−1.717
	8	−0.679	−0.668	−1.244	−1.229	−1.923	−1.897
	9	−0.773	−0.762	−1.289	−1.278	−2.062	−2.040
	10	−0.863	−0.854	−1.330	−1.321	−2.193	−2.175
	11	−0.952	−0.944	−1.358	−1.349	−2.310	−2.293
$1s^22s^22p^3(^2P)$	6	−0.602	−0.624	−0.538	−0.538	−1.140	−1.162
	7	−0.938	−0.953	−0.616	−0.594	−1.554	−1.547
	8	−1.155	−1.174	−0.665w	−0.642	−1.820	−1.816
	9	−1.340	−1.362	−0.706	−0.686	−2.046	−2.048
	10	−1.510	−1.533	−0.736	−0.717	−2.246	−2.250
	11	−1.673	−1.697	−0.758	−0.742	−2.431	−2.439

gives the degree of decoupling of $\chi_{\rm int}$ and χ_F. Some $E_{\rm int}$ and E_F values from the three different calculations are compared in Table III. The two correlations are decoupled to within 0.02 eV.

The $E_{\rm int}$ and E_F values reported in Tables IV–VII are from the total CI $[\phi_{\rm RHF} \leftrightarrow (\chi_{\rm int}+\chi_F)]$ and do not include any $\chi_{\rm int} \leftrightarrow \chi_F$ coupling error. $E_{\rm int}$ values of Table I were taken from the separate $\chi_{\rm int}$ CI $(\phi_{\rm RHF} \leftrightarrow \chi_{\rm int})$ to make a more meaningful comparison with the values of Refs. 7 and 20 which consider $\chi_{\rm int}$ alone.

Of course, our attempt to calculate $\chi_{\rm int}+\chi_F$

TABLE IV. Breakdown of the correlation energy (in eV) into its three components for various species of B and C. These values are from total CI, $\phi_{\rm RHF} \leftrightarrow (\chi_{\rm int}+\chi_F)$ (see text). $E_{\rm CORR}$("expt") is the "experimental" correlation energy (see text); $E_{\rm int}$ is the internal correlation energy; E_F is the polarization plus semi-internal correlation energy; and E_u("expt") $= E_{\rm CORR}$("expt") $- (E_{\rm int}+E_F)$ is the "experimental" all-external correlation energy (see text). The notation (–) indicates that $E_{\rm CORR}$("expt") is not available through lack of experimental data.

	$Z=5$				$Z=6$			
Species	$E_{\rm CORR}$("expt")	$E_{\rm int}$	E_F	E_u("expt")	$E_{\rm CORR}$("expt")	$E_{\rm int}$	E_F	E_u("expt")
$1s^22s^22p\ ^2P$	−3.40	−0.802	−0.586	−2.01	−3.78	−1.088	−0.662	−2.03
$1s^22s^22p^2\ ^3P$	(–)	−0.259	−0.760	(–)	−4.30	−0.465	−1.014	−2.82
^1D	(–)	−0.214	−0.790	(–)	−4.60	−0.438	−1.032	−3.13
^1S	(–)	−0.980	−0.261	(–)	−5.41	−1.626	−0.138	−3.65
$1s^22s^22p^3\ ^4S$					(–)	0	−1.022	(–)
^2D					(–)	0	−1.065	(–)
^2P					(–)	−0.624	−0.538	(–)
$1s^22s2p\ ^3P$	−1.60	0	−0.150	−1.45	−1.63	0	−0.154	−1.47
^1P	−2.77	0	−0.972	−1.80				
$1s^22s2p^2\ ^4P$					−2.03	0	−0.139	−1.89
^2D					−3.43	0	−1.119	−2.31
^2S					−3.44	0	−0.316	−3.12
^2P					−3.99	0	−1.511	−2.48

TABLE V. Same as Table IV for various species of N and O.

	$Z=7$				$Z=8$			
Species	E_{CORR}("expt")	E_{int}	E_F	E_u("expt")	E_{CORR}("expt")	E_{int}	E_F	E_u("expt")
$1s^22s^22p\ ^2P$	−4.11	−1.313	−0.714	−2.08	−4.41	−1.522	−0.747	−2.14
$1s^22s^22p^2\ ^3P$	−4.54	−0.580	−1.135	−2.83	−4.76	−0.679	−1.204	−2.88
^1D	−4.90	−0.564	−1.153	−3.18	−5.17	−0.668	−1.229	−3.27
^1S	−5.96	−2.148	−0.070	−3.74	−6.42	−2.571	−0.046	−3.80
$1s^22s^22p^3\ ^4S$	−5.12	0	−1.278	−3.84	−5.25	0	−1.397	−3.85
^2D	−5.66	0	−1.314	−4.35	−5.80	0	−1.446	−4.35
^2P	−6.31	−0.953	−0.594	−4.76	−6.58	−1.174	−0.642	−4.76
$1s^22s^22p^4\ ^3P$	(–)	0	−0.818	(–)	−7.02	0	−1.036	−5.98
^1D	(–)	0	−0.933	(–)	−7.32	0	−1.091	−6.23
^1S	(–)	−1.099	−0.101	(–)	−8.33	−1.500	−0.041	−6.79
$1s^22s^22p^5\ ^2P$					(–)	0	−0.551	(–)
$1s^22s2p\ ^3P$	−1.72	0	−0.154	−1.57	−1.82	0	−0.155	−1.67
^1P	−3.06	0	−1.112	−1.95	−3.14	0	−1.132	−2.01
$1s^22s2p^2\ ^4P$	−2.11	0	−0.144	−1.97	−2.28	0	−0.147	−2.13
^2D	−3.53	0	−1.132	−2.40	−3.66	0	−1.137	−2.52
^2S	−3.40	0	−0.180	−3.22	−3.43	0	−0.144	−3.28
^2P	−4.14	0	−1.598	−2.54	−4.32	0	−1.641	−2.68
$1s^22s2p^3\ ^5S$	−2.55	0	0	−2.55	−2.72	0	0	−2.72
^3D	−4.40	0	−1.211	−3.19	−4.55	0	−1.222	−3.32
^3P	−4.45	0	−0.735	−3.71	−4.52	0	−0.664	−3.86
^1D	−6.00	0	−2.416	−3.58	−6.07	0	−2.391	−3.67
^3S	−5.37	0	−1.891	−3.48	−5.51	0	−1.975	−3.54
^1P	−5.30	0	−1.344	−3.96	−5.88	0	−1.426	−4.45
$1s^22s2p^4\ ^4P$	−5.47	0	−0.978	−4.49	−5.63	0	−0.935	−4.70
^2D	(–)	0	−2.011	(–)	−7.03	0	−1.957	−5.07
^2S					−7.00	0	−1.164	−5.83
^2P					−7.96	0	−2.523	−5.43
$1s^22s2p^5\ ^3P$					−8.54	0	−1.947	−6.59
$1s^22p^2\ ^3P$	−1.88	0	0	−1.88	−1.93	0	0	−1.93
^1D	−2.92	0	−0.925	−1.99	−2.99	0	−0.887	−2.11
^1S[a]	−1.10	−2.192	−0.209	−3.08	−0.851	−2.543	−0.207	−3.19

[a] This species is the only one in our calculations where another state with lower energy but the same symmetry and N exists ($1s^22s^2\ ^1S$). For this reason it could not be treated by total CI by our program, and the reported values of E_{int} and E_F are from separate CI; $\phi_{\mathrm{RHF}} \longleftrightarrow \chi_{\mathrm{int}}$ and $\phi_{\mathrm{RHF}} \longleftrightarrow \chi_F$ (see text).

TABLE VI. Same as Table IV for various species of F and Ne.

	$Z=9$				$Z=10$			
Species	E_{CORR}("expt")	E_{int}	E_F	E_u("expt")	E_{CORR}("expt")	E_{int}	E_F	E_u("expt")
$1s^22s^22p\ ^2P$	−4.71	−1.723	−0.771	−2.22	−4.95	−1.920	−0.789	−2.24
$1s^22s^22p^2\ ^3P$	−4.95	−0.772	−1.249	−2.93	−5.12	−0.862	−1.281	−2.98
^1D	−5.39	−0.762	−1.278	−3.35	−5.61	−0.854	−1.321	−3.44
^1S	−6.91	−2.955	−0.032	−3.92	−7.35	−3.320	−0.026	−4.00
$1s^22s^22p^3\ ^4S$	−5.36	0	−1.465	−3.90	−5.44	0	−1.515	−3.93
^2D	−5.90	0	−1.530	−4.37	−6.04	0	−1.587	4.45
^2P	−6.83	−1.362	−0.686	−4.78	−7.10	−1.533	−0.717	−4.85
$1s^22s^22p^4\ ^3P$	−7.07	0	−1.127	−5.94	−7.27	0	−1.186	−6.08
^1D	−7.40	0	−1.181	−6.22	−7.59	0	−1.242	−6.35
^1S	−8.57	−1.801	−0.014	−6.75	−8.95	−2.059	−0.004	−6.89
$1s^22s^22p^5\ ^2P$	−8.82	0	−0.625	−8.20	−8.92	0	−0.672	−8.25
$1s^22s^2p^5\ ^3P$	−8.08	0	−1.818	−6.26				
^1P	−9.18	0	−2.692	−6.49				
$1s^22s2p^6\ ^2S$					−12.19	0	−2.661	9.53

TABLE VII. Same as Table IV for various species of Na ($Z=11$).

Species	E_{CORR}("exp")	E_{int}	E_F	E_u("expt")
$1s^22s^22p\ ^2P$	−5.20	−2.115	−0.804	−2.28
$1s^22s^22p^2\ ^3P$	−5.25	−0.950	−1.305	−3.00
^1D	−5.88	−0.944	−1.349	−3.59
^1S	−7.81	−3.672	−0.023	−4.11
$1s^22s^22p^3\ ^4S$	−5.52	0	−1.549	−3.97
^2D	−6.18	0	−1.629	−4.55
^2P	−7.37	−1.697	−0.742	−4.93
$1s^22s^22p^4\ ^3P$	−7.46	0	−1.227	−6.23
^1D	−7.78	0	−1.284	−6.50
^1S	−9.33	−2.296	−0.000	−7.035
$1s^22s^22p^5\ ^2P$	−9.14	0	−0.702	−8.44
$1s^22s2p^6\ ^2S$	−12.08	0	−2.256	−9.557

without considering χ_u introduces a second decoupling assumption; the decoupling of χ_u and $\chi_{\mathrm{int}}+\chi_F$. However, as shown by the recent calculations of Yin and Silverstone[28] on 2^1P He and 2^3P He, this coupling is expected to be of the order of the energy contributions of single excitations in closed shells. The latter are known to be small.[5]

IV. "EXPERIMENTAL" AND ALL-EXTERNAL CORRELATION ENERGIES

The total correlation energy is defined as

$$E_{\mathrm{CORR}}=E_{\mathrm{tot}}-(E_{\mathrm{RHF}}+E_{\mathrm{REL}}), \tag{24}$$

where E_{REL} is the relativistic energy including spin-orbit coupling. Total energies of atoms and ions E_{tot} can be obtained using the experimental ionization potentials reported in Moore's[29] tables. RHF energies for many species are reported in the literature[21–24] or can be calculated using available programs. These E_{RHF} are calculated assuming infinite nuclear mass and must be multiplied by $1-m_e/M_n$ for "elementary mass correction."[30] E_{REL} is the hardest to calculate. Silverman, Scherr, and Matsen[31] using a semiempirical procedure obtain estimates of relativistic energy for closed shells. Assuming orbital additivity for E_{REL} and calculating spin-orbit coupling contributions using experimental term level energies[29] and the Landé splitting rule, fair estimates of the relativistic energy are obtained. Thus we get all terms on the right-hand side of Eq. (24) and obtain the so-called "experimental" correlation energy. The reason for writing "experimental" in quotes is the semiempirical nature of this quantity.

Clementi used the procedure outlined above to get correlation energies of ground configurations.[32] He estimates an error of about 5% for $Z<10$ and 10% for $Z>10$ (e.g., ~0.6 eV for neutral Ne). E_{CORR} for $1s^22s2p^n$ and $1s^22p^2$ configurations were calculated by one of us (Ï. Ö.) for this work. The "experimental" all-external energy E_u ("expt") is now obtained from

$$E_u(\text{"expt"})=E_{\mathrm{CORR}}(\text{"expt"})-E_{\mathrm{int}}+E_F). \tag{25}$$

A breakdown of the total correlation energy into its three components for various species of B, C, N, O, F, Ne, and Na is shown in Tables IV–VII which constitute a summary of our calculations. The error in the "experimental" energy is of course carried over into E_u. The all-external correlation energies reported in these tables are therefore less reliable and are given to fewer digits than E_{int} and E_F. E_{int} is seen to carry most of the Z dependence of the total correlation energy. The approximate transferability of E_u along Z for a given isoelectronic sequence is apparent. Transferability of all-external pair energies among ions, configurations, and symmetry states of a given Z will be discussed in Paper II.

The three kinds of correlation energy are plotted for ground states of first-row atoms in Fig. 3. The internal correlation energy decreases linearly with the number of added $2p$ electrons with parallel spin.[7] E_F is dependent on the number of vacancies in the HF sea as well as on the number of electrons. Therefore it makes a maximum at nitrogen where the holes and particles in the $2p$ subshell are balanced. The decrease to the left is due to decreasing N while the decrease in the number of holes is responsible for the decrease to the right. The all-external correlation energy E_u is seen to increase smoothly with the added electrons.

Each CI computation gave a detailed wave function including all the "specific" correlation effects.[33] The CI wave function for $1s^22s^22p^2\ ^1D$ carbon is reported in Table VIII as an example. The HF wave functions for closed shells are known to reproduce charge densities quite ac-

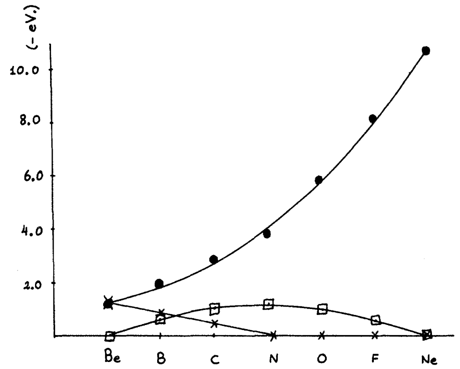

FIG. 3. Three kinds of correlation in ground states of neutral first-row atoms. E_{int} is the internal correlation energy (×), E_F is the polarization plus semi-internal correlation energy (□), and E_u is the all-external correlation energy (●).

curately. The similarity of χ_u to χ of closed shells suggests that $\phi_{\mathrm{RHF}}+\chi_{\mathrm{int}}+\chi_F$ might have the same property. Calculations of transition probabilities using the wave functions of this work will be reported in Paper III of this series.

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TABLE VIII. CI wave function for $1s^22s^22p^2\,{}^1D$ carbon. $\mathcal{A}$ is the antisymmetrizer. Each determinant is followed by its coefficient (in the $\langle\phi_{\mathrm{RHF}}|\phi_{\mathrm{RHF}}\rangle=1$ normalization convention) and its contribution to the energy (see Ref. 15 of text). Note that the sum of all contributions (−1.470 eV) is rigorously equal to $\Delta E_{\mathrm{CI}}=E_{\mathrm{CI}}-E_{\mathrm{RHF}}$, where $E_{\mathrm{CI}}=-1025.398$ eV and $E_{\mathrm{RHF}}=-1023.928$ eV; any apparent discrepancy is due to roundoff error. The "renormalization factor," which is the coefficient of ϕ_{RHF} when $\langle\phi_{\mathrm{RHF}}+\chi_{\mathrm{int}}+\chi_F|\phi_{\mathrm{RHF}}+\chi_{\mathrm{int}}+\chi_F\rangle=1$, has the value 0.980101. Bar on an orbital indicates β spin; no bar indicates α spin.

	Determinant	Coefficient	Contribution (eV)
	$\phi_{\mathrm{RHF}}=\mathcal{A}(1s1\bar{s}2s2\bar{s}2p_+2\bar{p}_+)$	1.000 000	−1023.928
$\hat{f}_{2s2s;\,2p}$	$\Delta_1=\mathcal{A}(1s1\bar{s}2p_-3\bar{p}_+2\bar{p}_+2\bar{p}_+)$	0.011 954	−0.012
	$\Delta_2=\mathcal{A}(1s1\bar{s}2\bar{p}_-3p_+2p_+2\bar{p}_+)$	−0.011 954	−0.012
	$\Delta_3=\mathcal{A}(1s1\bar{s}2p_03\bar{p}_02p_+2\bar{p}_+)$	−0.011 742	−0.012
	$\Delta_4=\mathcal{A}(1s1\bar{s}2\bar{p}_03p_02p_+2\bar{p}_+)$	−0.011 742	−0.012
$\hat{f}_{2s2p;\,2p}$	$\Delta_5=\mathcal{A}(1s1\bar{s}2p_-2\bar{s}3d_{++}2\bar{p}_+)$	−0.031 225	−0.058
	$\Delta_6=\mathcal{A}(1s1\bar{s}2p_02\bar{s}3d_+2\bar{p}_+)$	−0.017 570	−0.023
	$\Delta_7=\mathcal{A}(1s1\bar{s}2p_-2\bar{s}2p_+3\bar{d}_{++})$	−0.060 423	−0.203
	$\Delta_8=\mathcal{A}(1s1\bar{s}2\bar{p}_-2\bar{s}2p_+3d_{++})$	−0.029 199	−0.044
	$\Delta_9=\mathcal{A}(1s1\bar{s}2p_02\bar{s}2p_+3\bar{d}_+)$	−0.043 022	−0.102
	$\Delta_{10}=\mathcal{A}(1s1\bar{s}2\bar{p}_02\bar{s}2p_+3d_+)$	−0.025 452	−0.027
	$\Delta_{11}=\mathcal{A}(1s1\bar{s}2s2p_-3\bar{d}_{++}2\bar{p}_+)$	−0.029 199	−0.044
	$\Delta_{12}=\mathcal{A}(1s1\bar{s}2s2\bar{p}_-3\bar{d}_{++}2\bar{p}_+)$	0.060 423	−0.203
	$\Delta_{13}=\mathcal{A}(1s1\bar{s}2s2\bar{p}_03d_+2\bar{p}_+)$	0.025 452	−0.027
	$\Delta_{14}=\mathcal{A}(1s1\bar{s}2s2p_03\bar{d}_+2\bar{p}_+)$	0.043 022	−0.102
	$\Delta_{15}=\mathcal{A}(1s1\bar{s}2s2\bar{p}_-2p_+3\bar{d}_{++})$	0.031 225	−0.058
	$\Delta_{16}=\mathcal{A}(1s1\bar{s}2s2\bar{p}_02p_+3\bar{d}_+)$	−0.017 570	−0.023
$\hat{f}_{2p2p;\,2p}$	$\Delta_{17}=\mathcal{A}(1s1\bar{s}2s2\bar{s}2p_-4\bar{f}_{+++})$	0.034 569	−0.025
	$\Delta_{18}=\mathcal{A}(1s1\bar{s}2s2\bar{s}2\bar{p}_-4f_{+++})$	−0.034 570	−0.025
	$\Delta_{19}=\mathcal{A}(1s1\bar{s}2s2\bar{s}2p_04\bar{f}_{++})$	−0.020 005	−0.008
	$\Delta_{20}=\mathcal{A}(1s1\bar{s}2s2\bar{s}2\bar{p}_04\bar{f}_{++})$	0.020 005	−0.008
$\hat{f}_{2s}$	$\Delta_{21}=\mathcal{A}(1s1\bar{s}3d_02\bar{s}2p_+2\bar{p}_+)$	0.004 505	−0.001
	$\Delta_{22}=\mathcal{A}(1s1\bar{s}2s3\bar{d}_02p_+2\bar{p}_+)$	0.004 505	−0.001
$\hat{f}_{2p}$	$\Delta_{23}=\mathcal{A}(1s1\bar{s}2s2\bar{s}4f_+2\bar{p}_+)$	0.008 947	−0.002
	$\Delta_{24}=\mathcal{A}(1s1\bar{s}2s2\bar{s}2p_+4\bar{f}_+)$	0.008 947	−0.002
χ_{int}	$\Delta_{25}=\mathcal{A}(1s1\bar{s}2p_02\bar{p}_02p_+2\bar{p}_+)$	−0.143 152	−0.438

$\alpha_{3s}=\alpha_{3p}=\alpha_{3d}=2.12,\quad \alpha_{4f}=0.6\times2.12=1.272$

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[15] If $\langle\phi_0|\tilde{\chi}\rangle=0$ and $\langle\phi_0|\phi_0\rangle=1$, then

$$\mathcal{H}|\phi_0+\tilde{\chi}\rangle=E_{\phi_0+\tilde{\chi}}|\phi_0+\tilde{\chi}\rangle,$$

and $E_{\phi_0+\chi}=\langle\phi_0|\mathcal{H}|\phi_0\rangle+\langle\phi_0|\mathcal{H}|\tilde{\chi}\rangle$.

These expressions are true for the exact χ and $\mathcal{H}$. But they are also true for any $\tilde{\chi}$ as long as the above orthogonality and normalization conditions hold. Then $\mathcal{H}$ is no longer the exact Hamiltonian but a finite or infinite matrix in the space of $\phi_0+\tilde{\chi}$ and $E_{\phi_0+\tilde{\chi}}$ its eigenvalue in that subspace. If $\tilde{\chi}$ is made of a linear combination of various terms, $\tilde{\chi}=\Sigma_i\tilde{\chi}_i$, the energy can be analyzed into contributions E_i coming from the individual χ_i by

$$E=\langle\phi_0|\mathcal{H}|\phi_0\rangle+\sum_i\langle\phi_0|\mathcal{H}|\tilde{\chi}_i\rangle$$

and $E_i=\langle\phi_0|\mathcal{H}|\tilde{\chi}_i\rangle$. This expression was used to separate E_{int} and E_F from total E_{CI} in Tables II and IV–VII, various contributions to E_F in Table III, and contributions of individual determinants in Table VIII.

[16] HF sea is defined as all the occupied orbitals of the problem plus all the vacant ones that would complete the species into the next closed-shell configuration. For the first row all 1*s*, 2*s*, and 2*p* orbitals, occupied or unoccupied, define the HF sea.

[17] If an electron function $F(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_i,\ldots,\vec{x}_n)$ is "outside" the HF sea then

$$\langle i|F\rangle_{\vec{x}_i}=\int i^*(\vec{x}_i)\,F(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_i,\ldots,\vec{x}_n)\,d\vec{x}_i=0,$$

where $i\,(\vec{x}_i)$ is any HF sea orbital and integration is over $\vec{x}_i$ only.

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[25] In the anonymous-parentage approximation all correlation functions of Eqs. (16) and (20) are assumed to be independent of their parent HF determinant;

$$\hat{u}^K_{k_ak_b}=\hat{u}^L_{k_ak_b},\quad \hat{f}^K_{k_a}=\hat{f}^L_{k_a},$$

$$\hat{f}^K_{k_ak_b;1}=\hat{f}^L_{k_ak_b},\ \text{etc., for all } K \text{ and } L.$$

[26] Our CI program is "automatic" in the sense that the only inputs necessary are the analytic RHF orbitals, types of virtual orbitals to be included, and the coefficients C_k of $\phi_{\text{RHF}}=\Sigma_k C_k\Delta_k$. The program then finds the determinants that will mix (Ref. 27) using vector-coupling rules, constructs the CI matrix, determines the integrals necessary for the evaluation of each matrix element, computes the integrals (I, R^k and c^k), optimizes the exponents of virtual STO, and prints out the results in the form given in Table VIII.

[27] The term "mix" is used in this paper in a limited sense, i.e., a function F is said to mix with ϕ_{RHF} if $\langle\phi_{\text{RHF}}|\mathcal{H}|F\rangle\neq 0$. If "mixing" is used to mean "making a nonzero contribution to the CI energy," then the definition above is only true for 2 × 2 CI. Two functions F, F' might contribute to the CI even if

$$\langle\phi_{\text{RHF}}|\mathcal{H}|F\rangle=\langle\phi_{\text{RHF}}|\mathcal{H}|F'\rangle=0,$$

but $\langle F|\mathcal{H}|F'\rangle\neq 0$. Such additional "semi-internal" terms that could mix indirectly and contribute to the energy shift are expected to be very small here, as some of the test calculations mentioned suggest.

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[33] These detailed CI wave functions have been deposited with the Superintendent of Documents, Library of Congress, Washington, D.C.