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Theory of Atomic Structure Including Electron Correlation. II. All-External Pair Correlations in the Various States and Ions of B, C, N, O, F, Ne, and Na, and Prediction of Electron Affinities and Atomic Excitation Energies

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The first paper of this series showed that the portion of the total correlation energy, which remains after two types of correlation effects specific to N (number of electrons), symmetry state, and Z are taken out, is quite similar in nature to correlation in closed shells. This remainder, the "all-external energy" is expected to be by and large made up of pair correlations whose values are transferable through N, symmetry state, and Z as predicted in the theory by Sinanoğlu. The present paper analyzes the all-external correlation energies of B, C, N, O, F, Ne, and Na into their irreducible all-external pair components. The predicted additivity and transferability of all-external pairs are found to hold within the error limits of experimental correlation energies. A set of such pair-correlation values applicable to a great many states and ions of $1s^n 2s^m 2p^k$ type are obtained. Together with the calculated values of the two other types of correlation effects, these yield nonrelativistic atomic energies to a root-mean-square deviation of 0.05 eV. A semiempirical method for the prediction of atomic energy levels of general nonclosed-shell species, excited configurations and states as well as ground states is presented. The method is applied to predictions of electron affinities, excited states of negative ions, excitation energies, intermultiplet separations, and term-splitting ratios. Results of the method are compared with experiment and other semiempirical and nonempirical methods.

I. INTRODUCTION

In the first paper of this series,[1] hereafter referred to as I, a theory of electron correlation for general nonclosed shells was outlined. The theory is applicable to excited states and configurations as well as ground states. Three mathematically and physically different correlation effects, (1) "internal," (2) "polarization and semi-internal," and (3) "all-external" correlations, were distinguished. The first two are unique to nonclosed shells and specific to each N (number of electrons), symmetry state, and Z. They are however calculable by finite configuration interaction (CI). Calculations of energy contributions and wave functions of these two specific effects 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 ions were performed and reported in I. The third effect, all-external correlation, is quite similar in nature to correlations in closed shells. The theory by Sinanoğlu entitled "Many Electron Theory of Atoms and Molecules" (MET)[2] predicts it to consist to a large extent of decoupled pair correlations. The all-external pairs are also predicted to be approximately (1) transferable, i.e., insensitive to N, symmetry state, and to a lesser extent Z; and (2) pairwise additive (weighted by group-theoretical pair-parentage coefficients) in reproducing total all-external correlation energies.

In this paper, the all-external energies of species treated in I are analyzed into all-external pair-correlation energies. Pair-correlation values applicable to a wide variety of excited states, configurations, and ions are reported. Approximate transferability and additivity predictions of MET for these pair energies are investigated and tested out. They are seen to be good approximations within the error limits of presently available "experimental" correlation energy data. Finally a semiempirical method, based on the present theory, for the prediction of atomic energy levels is presented. The method is applied to predictions of electron affinities, energies of excited states of negative ions, excitation energies, intermultiplet separations, and term-splitting ratios. The predictions agree well with experiment and demonstrate the method which goes beyond the previously available semiempirical and nonempirical theories.

II. ALL-EXTERNAL CORRELATION ENERGY AND ALL-EXTERNAL PAIR ENERGIES

The total energy of a nonclosed-shell atom was given in I as

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

$$\text{i.e.,}\ E \cong E_{\text{RHF}} + E_{\text{int}} + E_F + E_u ; \tag{1}$$

where χ_{int} and E_{int}, χ_F and E_F, χ_u and E_u are, respectively, the internal, polarization plus semi-internal, and all-external correlation wave functions and energies. The all-external correlation function χ_u in the unlinked-cluster approximation[2,3] is

$$\chi_u \cong \sum_{K>1}^{K} \chi_u^{K} = \sum_{K>1}^{K} C_K \left[\mathcal{A}(k_1 k_2 \cdots k_N) \times \left(2^{-\frac{1}{2}} \sum_{a>b} \frac{\hat{u}^{K}_{k_a k_b}}{k_a k_b} + \{\text{u. c.}\} \right) \right] , \tag{2}$$

$\{\text{u. c.}\} \equiv \{$unlinked clusters of $\hat{u}$'s in the "MET" sense$\}$,

and the all-external energy E_u is given by

$$E_u \cong \langle \Phi_{\text{RHF}} | \mathcal{H} | \chi_u \rangle = \sum_{K,L}^{K} C_K C_L \langle \Delta_K | \mathcal{H} | \chi_u^{L} \rangle . \tag{3}$$

MET predicts the all-external pair functions to be "dynamical"; that is, quite insensitive to "environment." Hence we can expect the $\hat{u}_{ij}^{K}$ to be independent of the parent determinant Δ_K or to use some average $\hat{u}_{ij}$ to a good approximation. With this "anonymous parentage"[3] approximation, Eq. (3) becomes

$$E_u \simeq \sum_{i>j}^{M} \rho_{ij} \epsilon_{ij} + \sum_{\{i>j\} \neq \{k>l\}} \rho_{ijkl} \epsilon_{ij;kl} , \tag{4}$$

where $\epsilon_{ij} = \langle \mathcal{B}(ij) | g_{12} | \hat{u}_{ij} \rangle$;

$$\epsilon_{ij;kl} = \langle \mathcal{B}(ij) | g_{12} | \hat{u}_{kl} \rangle . \tag{5}$$

ϵ_{ij} and $\epsilon_{ij;kl}$ are respectively pair and "cross-pair" correlation energies. $\mathcal{B}$ is the two-electron antisymmetrizer, and $g_{12} \equiv 1/|r_{12}|$. ρ_{ij} and $\rho_{ij;kl}$ are occupation probabilities of pairs i,j and cross-pairs $ij;kl$ of orbitals ($\rho_{ij;kl}$ includes cross-pairs like $\rho_{ij;il}$):

$$\rho_{ij} = \sum_{\substack{K \\ i,j \in K}} |C_K|^2$$

$$\text{and}\ \rho_{ij;kl} = \sum_{\substack{K \neq L \\ i,j \in K \\ k,l \in L}} (-1)^{\sigma} C_K^{*} C_L , \tag{6}$$

where σ is the number of permutations necessary to bring the $N-2$ spin orbitals of L (excluding k, l) into correspondence with the same orbitals in K (excluding i, j). If Δ_K and Δ_L have less than $N-2$ orbitals in common, the corresponding internal in Eq. (3) vanishes.

If the Hartree-Fock (HF) orbitals are given in the x, y, z ($p_x, p_y, p_z, d_{xx}, \ldots$, etc.) or in symmetry orbital ($p_+, p_0, p_-, d_{++}, \ldots$, etc.) bases [$\mathcal{B}(ij)$ type pairs], the cross-pairs are present in the total E_u expressions and may be comparable in magnitude with the ϵ_{ij}. Most of the cross-pairs vanish when the $\{\mathcal{B}(ij)\}$ basis is transformed into the irreducible pair basis $\{\psi_I^{\text{irr}}\}$:

$$\{\psi_I^{\text{irr}}\} = T\{\mathcal{B}(ij)\} , \tag{7a}$$

$$\psi_I^{\text{irr}} = \sum_{i>j} T_{ij;I} \mathcal{B}(ij) . \tag{7b}$$

Here T is the transformation matrix. The irreducible pair functions are characterized by the quantum numbers of the atomic invariance group $G[=O_3 \otimes SU_2\ (\text{spin})]$:

$$I = (LSM_L M_S , l_1 s_1 , l_2 s_2) . \tag{8}$$

Since G commutes with g_{12}, irreducible cross-pairs $\epsilon_{I;I'}{}^{\text{irr}}$ will vanish if $I \neq I'$. Then

$$E_u \simeq \sum_I \beta_I \epsilon_I^{\text{irr}} \quad \text{(when all } I \text{ are distinct)}, \tag{9}$$

$$\text{where}\ \epsilon_I^{\text{irr}} = \langle \psi_I^{\text{irr}} | g_{12} | \hat{u}_I^{\text{irr}} \rangle , \tag{10}$$

$$\beta_I = \sum_{i>j}^{M} \rho_{ij} |T_{ij;I}|^2 + \sum_{\substack{i>j \\ \{i,j\} \neq \{k,l\}}}^{M} \sum_{k>l}^{M} \rho_{ijkl} T_{ij;I} T^{*}_{kl;I} . \tag{11}$$

The $\mathcal{B}(ij) \to \psi_I^{\text{irr}}$ transformation is sufficient to get rid of all cross pair terms in the total all-external correlation energy expression of $1s^r 2s^n 2p^m$ ($r, n = 0, 1, 2$; $m = 0, 1, 2, \ldots, 6$) species. The E_u expression is thus reduced to a linear combination of pair-correlation energy contributions, similar to those in closed shells but weighted by nonunity occupation probabilities (pair parentage coefficients).

III. EVALUATION, ADDITIVITY, AND TRANSFERABILITY OF ALL-EXTERNAL PAIR ENERGIES

A. Extraction of All-External Pair Energies From Experimental Correlation Energy Data

In I the quantities χ_{int} and E_{int}, and χ_F and E_F

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 were calculated by finite CI. The "experimental" all-external correlation energy of each case was then evaluated from

$$E_u(\text{“expt”}) = E_{\text{CORR}}(\text{“expt”}) - (E_{\text{int}} + E_F) \quad , \qquad (12)$$

using "experimental" total correlation energies $E_{\text{CORR}}(\text{“expt”})$,

$$E_{\text{CORR}}(\text{“expt”}) = E_{\text{tot}}(\text{“expt”}) - (E_{\text{RHF}} + E_{\text{REL}}) \quad . \qquad (13)$$

Total experimental energies E_{tot} are obtained from spectroscopic data and E_{REL} are estimates of the relativistic energy including spin-orbit coupling.

For a given Z, Eq. (12) with Eq. (9) give a set of linear equations for the irreducible all-external pair energies:

$$\{E_u(\text{“expt”}) \simeq \textstyle\sum_I \beta_I \epsilon_I^{\text{irr}}\} \quad . \qquad (14)$$

Let the number of unknown pairs be P and the number of species with known $E_u(\text{“expt”})$, that is the number of equations in (14), be D. For a given Z we always had $D > P$. Any linearly independent P of these D equations could be solved to get the ϵ_I^{irr}. However, the error in $E_u(\text{“expt”})$ would then be directly carried over to the pair-energy values. A better way is to perform a least-squares fit taking β_I as variables and ϵ_I^{irr} as unknown constants. This way the random error in $E_u(\text{“expt”})$ will be averaged out as available data increase.

For those Z where enough data were available (B, C, N, and O) two such least-squares analyses, one involving only ground configurations $1s^2$, $1s^2 2s$, $1s^2 2s^2$, $1s^2 2s^2 2p^n$ ($n = 1, 2, \ldots, 6$) and one using ground and some excited configurations $1s^2$, $1s^2 2s$, $1s^2 2s^2$, $1s^2 2s^2 2p^n$ ($n = 1, 2, \ldots, 6$), $1s^2 2s 2p^m$ ($m = 1, 2, 3$), were carried out. The ϵ_I^{irr} obtained from these calculations are reported in Table I. The ϵ's involving two orbitals are combinations of two pair energies; e.g.,

$$\epsilon(1s^2 \leftarrow 2s) = \tfrac{3}{2}\epsilon(1s2s; {}^3S) + \tfrac{1}{2}\epsilon(1s2s; {}^1S) \quad ,$$

$$\epsilon(1s^2 \leftarrow 2p) = \tfrac{3}{2}\epsilon(1s2p; {}^3P) + \tfrac{1}{2}\epsilon(1s2p; {}^1P) \quad .$$

$\epsilon(2s^2 \leftarrow 2p)$ cannot be separated into its ${}^3P$ and ${}^1P$ components without excited configuration data. The separation reported for ground configuration pairs of B, C, N, and O assumes the same $\epsilon(2s2p; {}^3P)/\epsilon(2s2p; {}^1P)$ ratio as in ground plus excited configuration pairs. In F, Ne, and Na where excited configuration data were insufficient, $\epsilon(2s2p; {}^3P) = -0.100$ eV was assumed. The small $\epsilon(2s^2)$ and $\epsilon(1s^2 \leftarrow 2p)$ all-external correlations were not included in the least-squares analysis in order not to have them swamped by the errors in $E_u(\text{“expt”})$. The $\epsilon(2s^2)$ was obtained from an extrapolation of

TABLE I. Irreducible all-external pair-correlation energies (in eV). Set I pairs are from ground configurations data only; set II pairs are from ground and excited configurations (see text). ϵ's involving three orbitals are combinations of two pairs. $\epsilon(1s^2 \leftarrow 2s) = \frac{3}{2}\epsilon(1s2s; {}^3S) + \frac{1}{2}\epsilon(1s2s; {}^1S)$ and $\epsilon(1s^2 \leftarrow 2p) = \frac{3}{2}\epsilon(1s2p; {}^3p) + \frac{1}{2}\epsilon(1s2p; {}^1P)$. The $\epsilon(1s^2 \leftarrow 2p)$ energy is from Kelly's value for oxygen (Ref. 6). The $\epsilon(2s^2)$ energy is obtained from an extrapolation of values given in Ref. 4 for $Z=5$ and Ref. 5 for $Z=7$ and $Z=10$.

		$\epsilon(1s^2)$	$\epsilon(1s^2 \leftarrow 2s)$	$\epsilon(1s^2 \leftarrow 2p)$	$\epsilon(2s^2)$	$\epsilon(2s2p; {}^3P)$	$\epsilon(2s2p; {}^1P)$	$\epsilon(2p^2; {}^3P)$	$\epsilon(2p^2; {}^1D)$	$\epsilon(2p^2; {}^1S)$
$Z=5$[a]	I	1.221	0.104	0.102	0.060	0.131	0.449	···	···	···
	II	1.204	0.104	0.102	0.060	0.120	0.412	···	···	···
$Z=6$	I	1.240	0.090	0.102	0.102	0.121	0.450	0.282	0.591	1.107
	II	1.223	0.090	0.102	0.102	0.141	0.524	0.120	0.400	1.062
$Z=7$	I	1.256	0.071	0.102	0.147	0.118	0.485	0.244	0.589	1.165
	II	1.228	0.071	0.102	0.147	0.134	0.548	0.196	0.478	1.174
$Z=8$	I	1.261	0.082	0.102	0.190	0.104	0.551	0.219	0.556	1.111
	II	1.314	0.082	0.102	0.190	0.106	0.490	0.239	0.526	1.181
$Z=9$	I	1.266	0.079	0.102	0.230	0.100[b]	0.592	0.201	0.541	1.106
$Z=10$	I	1.268	0.085	0.102	0.275	0.100[b]	0.596	0.192	0.563	1.133
$Z=11$	I	1.274	0.083	0.102	0.318	0.100[b]	0.642	0.168	0.594	1.149

[a] $2p^2$ correlations for $Z=5$ could not be obtained due to lack of experimental data for the negative ion and lack of RHF calculations for $1s^2 2s 2p^2$ configuration of B.

[b] $\epsilon(2s2p; {}^3P) = -0.100$ eV was assumed for $Z = 9, 10$, and 11 where $\epsilon(2s^2 \leftarrow 2p)$ could not be separated due to lack of RHF calculations for the excited configurations of these Z. The total $\epsilon(2s^2 \leftarrow 2p)$ value, $\epsilon(2s^2 \leftarrow 2p) = \frac{3}{2}\epsilon(2s2p; {}^3P) + \frac{1}{2}\epsilon(2s2p; {}^1P)$ is free from the error coming from this assumption.

the values given by Tuan and Sinanoğlu[4] for B and by McKoy and Sinanoğlu[5] for N and Ne. Kelly's[6] value $\epsilon(1s^2-2p)=-0.102$ eV for oxygen was used for all Z. For the same reason $\epsilon(1s^2-2s)$ value given for ground plus excited configuration pairs comes from the ground configuration set. [Excited configurations E_u("expt") is expected to contain a larger error than ground configuration's E_u("expt") (see next section). Thus the small $\epsilon(1s^2-2s)$ value which survives in ground-configuration least squares is swamped by the error in ground plus excited configuration fit.]

Pair values from the two fits do not agree as well for $Z=5$ and 6 as the agreement which is seen to be much better for $Z=7$ and 8. This can be explained by the number of E_u("expt") data used in each case. For $Z=5$ we had 4 ground and 2 excited configurations; and for $Z=6$ we had 7 ground and 4 excited configuration E_u("expt") data. For $Z=7$, however, 10 ground and 11 excited configuration E_u("expt") data were available. For $Z=8$ these numbers are respectively 13 and 11. The expected averaging out of the random errors in E_u("expt") occurs as data increase, the pairs from two different fits coming into better agreement. Note, however, that as far as giving an indication of the transferability and additivity of the pairs in ground and excited configurations, the standard deviations of the fits are the significant indicators.

The all-external pair-correlation energies of the present theory should not be confused with the "total pair" correlation energies of the single-determinantal ground-state MET.[2,5] Pair-correlation energies reported in the literature are usually of the latter type.

As shown in I for first-row species, virtual pair transition type processes are still dominant both in E_{int} and E_F although certain single-electron excitations are also included in these correlations. A single-determinantal ground-state MET total pair Γ includes contributions of these nondynamical internal and semi-internal type virtual pair transitions as well as the dynamical all-external pair excitations. For a ground-state species the relation between the total pair energy $\epsilon_{\text{tot}}^{\text{MET}}(\Gamma)$ and the all-external pair energy of the present theory, $\epsilon_{\text{all-ex}}^{\text{NCMET}}(\Gamma)$, is given by

$$\epsilon_{\text{tot}}^{\text{MET}}(\Gamma)=\epsilon_{\text{int}}^{\text{NCMET}}(\Gamma)+\epsilon_{\text{s-i}}^{\text{NCMET}}(\Gamma)+\epsilon_{\text{all-ex}}^{\text{NCMET}}(\Gamma) \quad (15)$$

(for single-determinantal ground states only).

Total $2s^2$ correlation energy for example includes contributions of $2s^2\rightarrow 2p2p'$ (internal) and $2s^2\rightarrow 2p\hat{f}_{2s^2;\,2p}$ (semi-internal) type virtual pair transitions as well as $2s^2\rightarrow\hat{u}_{2s^2}$ (all-external) excitations. The present theory does not treat the internal and semi-internal pair energies individually but calculates all specific effects in a single CI. However, separate contributions of internal and semi-internal type pair processes for single-determinantal cases can later be extracted from the total CI energy using a well-known theorem of CI, as done in I.

Comparison of some correlation energies of this work with CI values of Weiss[7] and perturbation theory results of Kelly[6] are given in Table II. These values are total pair correlations or sums of total pair correlations among certain groups of electrons. Weiss's pair values are CI energy increments obtained by adding successively, configurations corresponding to a certain pair correlation to a growing CI matrix. His energies are expected to include most of the internal and semi-internal contributions to pairs but to exclude significant portions of the slowly convergent all-external part. His values are also

TABLE II. Comparison of some of the "total-pair correlation" energies with some available nonempirical values. The symbols $1s$-$2s$, $2s$-$2p$, and $2p$-$2p$ indicate the total correlation between the indicated groups of electrons. In O, for example, $1s\text{-}2s\equiv 4\epsilon(1s^2-2s)$. PC gives the present calculation. Correlations reported here include all three types of effects ("total pairs"). The $2s^2$ correlation, for example, is the sum of all-external, internal, and semi-internal correlation energy contributions coming from $2s$-$2s$. All values are in ($-$eV).

	$Z=6$		$Z=6$		$Z=8$	
	$1s^22s^22p^2$	(^3P)	$1s^22s^22p^2$	(^1S)	$1s^22s^22p^4$	(^3P)
Correlation	Weiss[a]	PC	Weiss[a]	PC	Kelly[b]	PC
$1s^2$	···	···	···	···	1.192	1.261
$1s$-$2s$	···	···	···	···	0.171	0.164
$2s^2$	0.748	0.568	1.747	1.728	0.408	0.380
$2s$-$2p$	1.456	1.828	0.675	0.952	2.732	2.695
$2p$-$2p$	0.258	0.282	1.110	1.107	2.465	2.211

[a] CI values from Ref. 7. (These, however, are not exactly comparable pair correlations; cf. text.)

[b] Diagrammatic perturbation theory values from Ref. 6.

dependent on the order of inclusion of each pair process into the CI. They do not therefore correspond exactly to the decoupled pairs as such and are not expected to agree very closely. Kelly's values are obtained by diagrammatic perturbation theory.

B. Transferability and Additivity of All-External Pair Energies

Detailed results of the least-squares fits for ground plus excited configuration data of $Z=7$ and 8 are reported in Table III. Reasons for the observed deviations can be enumerated as follows:

(1) For $1s^2$, $1s^2 2s^2 2p^n$ ($n=0, 1, \ldots, 6$) configurations the available over-all "experimental" correlation energies are in error by about ±5–±10%. This error is mostly due to the estimates of the relativistic energy. It is carried over to the E_u("expt") as absolute error and is expected to be roughly ±0.1 eV for $Z=5$, ±0.2 eV for $Z=6$, ±0.25 eV for $Z=7$, ±0.35 eV for $Z=8$, ±0.5 eV for $Z=9$, ±0.7 eV for $Z=10$, and ±1 eV for $Z=11$.

(2) For $1s^2 2s 2p^n$ ($n=0, 1, 2, 3$) configurations, the orbital additivity assumption for the relativistic energy

$$E_{\mathrm{REL}}(1s^2 2s) = E_{\mathrm{REL}}(1s^2) + \tfrac{1}{2}[E_{\mathrm{REL}}(1s^2 2s^2) - E_{\mathrm{REL}}(1s^2)] \qquad (16)$$

adds to the error in (1).[8]

(3) Errors in E_{int} and E_F. Both of these quantities are accurate to about ±0.01 eV. This error can be neglected compared to (1) and (2).

(4) "Additivity and transferability assumptions for the irreducible all-external pair correlation energies." These assumptions are based on the notions of MET by Sinanoğlu,[2] and the accuracy of the least-squares fit provides a direct test for them.

In Table III, giving the fit for $Z=7$ and 8, respectively, 21 and 24 data points are fitted by 6 parameters – the $\epsilon(1s^2)$, $\epsilon(1s^2 - 2s)$, $\epsilon(2s2p; {}^3P)$,

TABLE III. Comparison of "experimental" all-external correlation energies with those obtained from the least-squares fit pair values (in eV). E_u("expt") gives the "experimental" all-external correlation energies (see text). E_u(calc) gives the all-external energies calculated from the irreducible all-external pair correlation energies obtained from the least-squares analysis of "experimental" all-external energy data. $\Delta E_u = E_u(\text{"expt"}) - E_u(\text{calc})$.

			$Z=7$			$Z=8$	
Species		E_u("expt")	E_u(calc)	ΔE_u	E_u("expt")	E_u(calc)	ΔE_u
$1s^2$	${}^1S$	1.23	1.23	0.00	1.24	1.31	0.07
$1s^2 2s$	${}^2S$	1.37	1.30	−0.07	1.39	1.40	0.01
$1s^2 2s^2$	${}^1S$	1.52	1.52	0.00	1.59	1.67	0.08
$1s^2 2s^2 2p$	${}^2P$	2.08	2.10	0.02	2.14	2.18	0.04
$1s^2 2s^2 2p^2$	${}^3P$	2.83	2.87	0.04	2.88	2.92	0.04
	${}^1D$	3.18	3.15	−0.03	3.27	3.21	−0.06
	${}^1S$	3.74	3.85	0.11	3.80	3.86	0.06
$1s^2 2s^2 2p^3$	${}^4S$	3.84	3.84	0.00	3.85	3.91	0.06
	${}^2D$	4.35	4.26	−0.09	4.35	4.34	−0.01
	${}^2P$	4.76	4.73	−0.03	4.76	4.77	0.01
$1s^2 2s^2 2p^4$	${}^3P$	...	...	...	5.98	5.92	−0.06
	${}^1D$	...	...	...	6.23	6.21	−0.02
	${}^1S$	...	...	...	6.79	6.86	0.07
$1s^2 2s 2p$	${}^3P$	1.57	1.54	−0.03	1.67	1.61	−0.06
	${}^1P$	1.95	1.95	0.00	2.01	1.99	−0.02
$1s^2 2s 2p^2$	${}^4P$	1.98	1.97	−0.01	2.13	2.05	−0.08
	${}^2D$	2.40	2.46	0.06	2.52	2.53	0.01
	${}^2S$	3.22	3.15	−0.07	3.28	3.19	−0.09
	${}^2P$	2.54	2.59	0.05	2.68	2.63	−0.05
$1s^2 2s 2p^3$	${}^5S$	2.55	2.60	0.05	2.72	2.74	0.02
	${}^3D$	3.19	3.23	0.04	3.32	3.36	0.04
	${}^3P$	3.71	3.69	−0.02	3.86	3.80	−0.06
	${}^1D$	3.58	3.64	0.06	3.67	3.75	0.08
	${}^3S$	3.48	3.42	−0.06	3.54	3.51	−0.03
rms of ΔE_u[a]				0.05			0.05

[a] Root mean square of errors $= [\sum_i^M (\Delta E_u^{\,i})^2/M]^{\frac{1}{2}}$.

$\epsilon(2s2p;{}^1P)$, $\epsilon(2p^2;{}^3P)$, $\epsilon(2p^2;{}^1D)$, and $\epsilon(2p^2;{}^1S)$ pair energies. The root-mean-square (rms) and maximum deviations are well within the error limits of the data (error sources 1 and 2 above). Hence the pair transferability and additivity predictions of MET are seen to be good approximations within the limits of error of the presently available "experimental" correlation energies.

IV. PREDICTION OF ATOMIC ENERGY LEVELS

The theory in I and the transferability and additivity of all-external pair energies demonstrated above lead to a relatively simple method for predictions of atomic energy levels.

To predict the experimentally unknown energies of certain species of a given Z, the procedure involves two phases:

(A) Evaluation of irreducible all-external pair energies. This phase has been carried out in I and this paper for $1s^l2s^n2p^m$ ($l, n = 0, 1, 2$; $m = 0, 1, \ldots, 6$) type configurations of $Z = 5$ through 11. The theory, however, is not restricted to these orbitals, and the method given in this section is applicable to other types of atomic species.

(B) Calculation of the experimentally unknown energies by essentially inverting the procedure of A.

The first phase deals with the experimentally known species of the given Z to extract the all-external pair energies and involves the following steps:

(1) Evaluate total "experimental" correlation energies for those species whose experimental energies are known. This involves (a) getting total experimental energies by adding spectroscopic ionization and excitation energies.[9] (b) Obtaining estimates of the relativistic energy. This step is the bottleneck in the accuracy of any nonrelativistic method at present. As mentioned in the discussion of errors in Sec. IIIB, most of the error comes from the presently available relativistic energy estimates.[10] (c) Obtaining RHF energies and functions either from the literature,[11] or using available programs.

(2) Calculate the internal (E_{int}) and polarization plus semi-internal (E_F) energies by finite CI. Once the "Hartree-Fock sea" of the nonclosed-shell species is specified, the E_{int} and E_F are defined. The HF sea includes all K- and L-shell orbitals for the first row, all K. L- and M-shell orbitals for the second. Near-degeneracy effects resulting from close-lying orbitals of two different shells may be important for more complex atoms. Subtraction of E_{int} and E_F from the "experimental" correlation energies will now yield the "experimental" all-external energies, E_u("expt").

(3) Apply a least-squares fit to the E_u("expt") to extract the transferable irreducible all-external pair energies.

The second phase can now be applied to get the unknown energies. The steps are as follows:

(1) Get the RHF energies and wave functions as in step 1 of the first phase.[11]

(2) Get the relativistic energy estimates.

(3) Calculate χ_{int}, E_{int}, χ_F, and E_F using the automatic CI programs prepared for this work (see Paper I).

(4) Obtain the all-external correlation energy by taking the correct linear combination of the irreducible all-external pair energies found in the first phase.

Adding (1), (2), (3), and (4) one gets the total energy.

In the next section this method is applied to predictions of electron affinities, energies of excited states of negative ions, excitation energies, intermultiplet separations, and term-splitting ratios.

V. APPLICATIONS

A. Electron Affinities

Electron affinity is defined as the energy difference between the ground state of the neutral atom and the ground state of the negative ion. A positive electron affinity indicates a stable negative ion. In Tables IV through VII, electron affinities of C, N, O, and F calculated with the present method are compared with experimental values and predictions of other theories. The results of the present method are seen to agree well with experiment. Usually the difference between our prediction and the measured electron affinity of a given experimental method is of the order of the difference among measurements of different experimental methods. The all-external pair correlation energies used in predicting the energies of negative ions are those obtained from the least-squares analysis of ground-configuration data. Since negative-ion data were not used in obtaining these pairs, our values are actual predictions and not the results of a best fit. The predictions themselves are accurate at best to within ± 0.1 eV as may be judged from the rms deviations in Table III.

B. Excited States of Negative Ions

Table VIII gives the energies of excited states of negative ions of C and N, relative to the ground states of the ions. Results of the present method are compared with those of restricted Hartree-Fock,[11] Layzer,[12] and values obtained by Bates and Moiseiwitsch[13] using an extrapolation technique. Extrapolation of the energy through a single isoelectronic sequence using three, four, or five parameter Z expansion formulas often

TABLE IV. Electron affinity of carbon atom.

	Experimental method	Electron affinity (eV)
This calculation[a]		1.17
Hartree-Fock (Ref. 11)		0.55
Layzer (Ref. 12)		6.77
Seman and Branscomb[b]	Photodetachment	1.25 ± 0.03
Lagergren[c]	Electron impact on CO	1.11 ± 0.05
Fineman and Petrocelli[d]	Electron impact on CO	1.33 ± 0.18
Honig[e]	Mass spectrometry	1.2

[a] Both the ground state of the neutral atom and the negative ion were calculated with the method of this paper.
[b] M. L. Seman and L. M. Branscomb, Phys. Rev. 125, 1602 (1962).
[c] C. R. Lagergren, Ph.D. thesis, University of Minnesota, 1955 (unpublished).
[d] M. A. Fineman and A. Petrocelli, Bull. Am. Phys. Soc. 3, 258 (1958).
[e] R. E. Honig, J. Chem. Phys. 22, 126 (1954).

TABLE V. Electron affinity of nitrogen atom.

	Electron affinity (eV)
This calculation[a]	−0.45
Hartree-Fock (Ref. 11)	−2.15
Layzer (Ref. 12)	4.82

[a] Both the ground state of the neutral atom and the negative ion were calculated with the method of this paper.

yield quite accurate energy predictions.[14] We therefore expect Bates and Moiseiwitsch's values to be close to the correct values. The all-external pairs used in our predictions are again from the ground-configuration fit.

Although Z-extrapolation methods as used by Bates and Moiseiwitsch,[13] Edlén,[14] and Edie and Rohrlich[15] are quite accurate, they require enough experimental information on an isoelectronic sequence to determine the parameters of the expansion formulas. Our method retains its predictive power even when there is little or no experimental information on the isoelectronic sequence under study. Z extrapolation methods are therefore of a different nature than ours, and for this reason we do not compare their predictions with those of the present theory. A semiempirical method developed by Rohrlich[16] improves the F and G parameter method by including additional physically meaningful parameters. But the predictive power is then restricted by the high number of empirical parameters which have to be obtained from a single configuration. In some cases (e.g., ground-state configuration of the first row) as many parameters may be involved as there are experimental data.

C. Excitation Energies

Table IX gives the energies of actual (spectroscopic) single and double excitations from ground states to various states of excited configurations. Our predictions are compared with those of

TABLE VI. Electron affinity of oxygen atom.

	Experimental method	Electron affinity (eV)
This calculation[a]		1.24
Hartree-Fock (Ref. 11)		−0.54
Layzer (Ref. 12)		6.46
Branscomb, Burch, Smith and Geltman[b]	Photodetachment	1.465 ± 0.005
Elder, Villarejo, and Inghram[c]	Photon impact on O_2	1.461 ± 0.024
Berry, Mackie, Taylor, and Lynch[d]	Radiative capture of electrons	1.478 ± 0.002

[a] Both the ground state of the neutral atom and the negative ion were calculated with the method of this paper.
[b] L. M. Branscomb, D. S. Burch, S. J. Smith, and S. Geltman, Phys. Rev. 111, 504 (1958).
[c] F. A. Elder, D. Villarejo, and M. G. Inghram, J. Chem. Phys. 43, 758 (1965).
[d] R. S. Berry, J. C. Mackie, R. L. Taylor, and R. Lynch, J. Chem. Phys. 43, 3067 (1965).

TABLE VII. Electron affinity of fluorine atom.

	Experimental method	Electron affinity (eV)
This calculation[a]		3.23
Hartree-Fock (Ref. 11)		1.36
Layzer (Ref. 12)		8.14
Berry and Reimann[b]	Photodetachment	3.448 ± 0.005
Cubicuotti[c]	Lattice energy	3.47 ± 0.04
Stamper and Borrow[d]	Dissociation of alkali fluorides	3.62 ± 0.1
Bernstein and Metley[e]	Magnetron	3.57 ± 0.17
Jortner, Stein, and Treinin[f]	Spectrophotometry	3.557 ± 0.086
Tandon, Bhutra, and Tandon[g]	Semiempirical (from dissociation energy of alkali fluorides)	3.843

[a] Both the ground state of the neutral atom and the negative ion were calculated with the method of this paper.

[b] R. S. Berry and C. W. Reimann, J. Chem. Phys. 38, 1540 (1963).

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Layzer,[12] Bacher and Goudsmit,[17] the *F* and *G* parameter method of Slater,[18] and experimental values. All-external pairs used in our predictions are again from the ground-configuration data. The average energies, *F* and *G* parameters used in Slater's theory, are empirical values obtained by a least-squares fit of experimental energies of the multiplets of each configuration. The Bacher and Goudsmit method is also empirical and uses the experimental energies of ions containing different numbers of electrons. The predictions of the present method are closer to experimental values more often than even those semiempirical theories which utilize much higher numbers of empirical parameters. (Our predictions are closer to experiment in 29 cases. Bacher and Goudsmit's theory gives better agreement in 4, the *F* and *G* parameter method in 12, and Layzer's theory in 2 cases.)

D. Intermultiplet Separations

Table X compares intermultiplet separations of excited configurations obtained with the present method with predictions of Bacher and Goudsmit, empirical *F* and *G* parameter method, Layzer's theory and experimental values. Our method is again seen to agree with experiment more often than the others (Bacher and Goudsmit's method is better in 6, the *F* and *G* parameter method in 9, Layzer's theory in 6, and the present method in 19 cases). The all-external pairs used in our calculations are again from the ground-configuration data.

TABLE VIII. Energies of excited states of negative ions. (All values in eV). Reported energies are relative to the ground state of the negative ion.

	Restricted Hartree-Fock (RHF) (Ref. 11)	Layzer (Ref. 12)	Present calculation	Bates and Moiseiwitsch (Ref. 13)
C ^4S	0	0	0	0
^2D	1.80	1.94	1.30	1.29
^2P	2.94	2.88	1.99	1.46
N ^3P	0	0	0	0
^1D	1.50	1.66	1.04	1.28
^1S	3.68	3.55	2.36	2.60

[a] All-external pair energies used in this calculation were obtained from ground-configuration data. These values are therefore actual predictions and not the results of a best fit.

TABLE IX. Exciation energies. (All values in eV.)

Excitation		Z	B. G. (Ref. 17)	F and G parameter method (Ref. 18)	Layzer (Ref. 12)	Present calculation[a]	Observed (Ref. 9)
$1s^2 2s^2 (^1S) \rightarrow 1s^2 2s 2p$	^3P	5	···	4.82	4.29	4.53	4.63
		7	···	9.58	7.82	8.39	8.34
		8	···	10.22	9.59	10.29	10.15
	^1P	5	···	8.54	8.24	9.02	9.10
		7	···	17.44	14.96	16.27	16.20
		8	···	19.69	18.32	19.72	19.69
$1s^2 2s^2 (^1S) \rightarrow 1s^2 2p^2$	^3P	7	···	21.55	22.54	21.97	21.75
		8	···	26.28	27.08	26.79	26.49
	D	7	···	24.08	25.28	23.39	23.42
		8	···	29.46	30.40	28.84	28.73
	^1S	7	···	27.87	30.85	29.67	29.18
		8	···	34.23	37.14	36.33	35.69
$1s^2 2s^2 2p (^2P) \rightarrow 1s^2 2s 2p^2$	^4P	6	5.92	5.27	6.56	5.16	5.33
		7	7.78	6.93	8.25	7.01	7.07
		8	9.83	8.75	9.94	8.93	8.77
	^2D	6	10.08	9.47	10.97	9.07	9.29
		7	13.42	12.73	14.03	12.35	12.51
		8	16.74	15.92	17.09	15.70	15.71
	^2S	6	14.62	11.59	13.66	12.04	11.96
		7	19.18	15.80	17.58	16.32	16.23
		8	23.70	19.91	21.50	20.55	20.35
	^2P	6	15.25	13.65	14.16	13.64	13.71
		7	19.64	18.19	18.24	18.03	18.06
		8	24.00	22.29	22.32	22.37	22.32
$1s^2 2s^2 2p^2 (^3P) \rightarrow 1s^2 2s 2p^3$	^5S	7	5.52	5.54	9.55	5.67	5.84
		8	7.18	7.22	11.19	7.58	7.45
	^3D	7	11.15	11.56	16.02	11.20	11.42
		8	14.57	14.98	19.31	14.85	14.85
	^3P	7	13.17	13.35	18.22	13.45	13.53
		8	17.22	17.36	22.09	17.79	17.63
	^1D	7	17.96	18.26	22.10	17.67	17.87
		8	23.10	23.41	26.99	23.07	23.16
	^3S	7	19.16	18.93	21.86	19.25	19.22
		8	24.25	24.07	26.69	24.46	24.41
	^1P	7	19.99	20.04	24.26	20.47	20.67
		8	25.75	25.78	29.72	26.35	26.07
$1s^2 2s^2 2p^3 (^4S) \rightarrow 1s^2 2s 2p^4$	^4P	7		10.81	19.66	10.86	10.92
		8	14.92	14.65	23.50	15.00	14.85
	^2D	8	20.74	20.60	29.67	20.55	20.58
	^2S	8	24.46	23.76	33.51	24.44	24.26
	^2P	8	26.55	26.15	34.22	26.57	26.35
$1s^2 2s^2 2p^4 (^3P) \rightarrow 1s^2 2s 2p^5$	^3P	8	···	19.13	29.68	15.44	15.64
		9	···	···	34.37	20.07	20.43
	^1P	9	···	···	42.55	28.80	29.69
$1s^2 2s^2 2p^5 (^2P) \rightarrow 1s^2 2s 2p^6$	^2S	10	···	···	47.10	26.10	26.88
		11	···	···	52.64	31.77	32.73

TABLE X. Intermultiplet separations. (All values in −eV.)

Separation	Z	B. G. (Ref. 17)	F and G parameter method (Ref. 18)	Layzer (Ref. 12)	Present calculation[a]	Observed (Ref. 9)
$1s^22s2p$ (^3P–^1P)	5	•••	3.72	3.95	4.50	4.47
	7	•••	7.86	7.14	7.88	7.86
	8	•••	9.47	8.73	9.44	9.54
$1s^22p^2$ (^3P–^1D)	7	•••	2.53	2.74	1.42	1.66
	8	•••	3.18	3.32	2.05	2.24
(^1D–^1S)	7	•••	3.79	5.57	6.28	5.76
	8	•••	4.77	6.75	7.49	6.97
(^3P–^1S)	7	•••	6.31	8.31	7.70	7.43
	8	•••	7.95	10.06	9.54	9.21
$1s^22s2p^2$ (^4P–^2P)	6	9.33	8.38	7.60	8.48	8.38
	7	11.86	11.27	9.99	11.02	11.00
	8	14.30	13.55	12.39	13.43	13.56
(^4P–^2D)	6	4.16	4.20	4.41	3.91	3.96
	7	5.64	5.80	5.78	5.35	5.45
	8	7.03	7.18	7.15	6.77	6.94
(^2D–^2P)	6	5.17	4.18	3.19	4.57	4.43
	7	6.21	5.46	4.21	5.67	5.55
	8	7.26	6.37	5.23	6.67	6.62
(^2D–^2S)	6	4.54	2.11	2.70	2.97	2.75
	7	5.76	3.07	3.56	3.96	3.72
	8	6.97	3.99	4.42	4.85	4.64
$1s^22s2p^3$ (^5S–^3S)	7	13.64	13.39	12.31	13.58	13.39
	8	17.06	16.85	15.50	16.88	16.96
(^5S–^3D)	7	5.63	6.02	6.47	5.52	5.59
	8	7.39	7.77	8.13	7.27	7.40
(^5S–^3P)	7	7.65	7.81	8.67	7.77	7.69
	8	10.03	10.14	10.90	10.21	10.17
(^3D–^3P)	7	2.02	1.78	2.20	2.25	2.11
	8	2.65	2.37	2.78	2.94	2.77
(^3D–^1D)	7	6.82	6.70	6.09	6.47	6.44
	8	8.53	8.43	7.68	8.21	8.31
(^3P–^1P)	7	6.82	6.70	6.04	7.02	7.14
	8	8.53	8.43	7.63	8.59	8.44
$1s^22s2p^4$ (^4P–^2P)	8	11.63	11.50	10.73	11.57	11.51
(^4P–^2D)	8	5.82	5.94	6.18	5.68	5.73
(^2D–^2S)	8	3.73	3.16	3.84	3.89	3.68
(^4P–^2S)	8	9.54	9.11	10.01	9.44	9.42
$1s^22s2p^5$ (^3P–^1P)	9	•••	•••	8.18	8.73	9.26

[a] All-external pair energies used in this calculation were obtained from ground-configuration data. These values are therefore actual predictions and not the results of a best fit.

E. Term-Splitting Ratios

Configurations involving orbitals of only s and p symmetry give rise to multiplets of S, P, and D symmetries. For a given configuration the ratio of energy differences between these symmetry states constitute a critical test for energy predictions. For configurations with single S, P, and D states ($1s^22p^2$, $1s^22s^22p^4$, etc.), the SD/DP term-splitting ratio is given by

$$SD/DP = [E(S) - E(D)]/[E(D) - E(P)] \quad . \qquad (17)$$

If more than one state of S, P, or D symmetry occurs within the same configuration ($1s^22s2p^2$, $1s^22s2p^3$, etc.), a multiplicity weighted average is taken over states of same $\vec{L}^2$ eigenvalue before the ratio is calculated. If $m_S{}^i$, $m_P{}^j$, and $m_D{}^k$ are multiplicities of the ith, jth, and kth states of S, P, and D symmetry, and N_S, N_P, and N_D are the number of S, P, and D states in the configuration, the term-splitting ratio is given by

$$\frac{(SD)}{(DP)} = \frac{\dfrac{\sum_i^{N_S} m_S^i E(^{m_S^i}S)}{\sum_i^{N_S} m_S^i} - \dfrac{\sum_k^{N_D} m_D^k E(^{m_D^k}D)}{\sum_k^{N_D} m_D^k}}{\dfrac{\sum_k^{N_D} m_D^k E(^{m_D^k}D)}{\sum_k^{N_D} m_D^k} - \dfrac{\sum_j^{N_P} m_P^j E(^{m_P^j}P)}{\sum_j^{N_P} m_P^j}} \quad . \qquad (18)$$

In the F and G parameter method average energies and the parameters cancel and the ratio is always 1.5, independent of Z and configuration. SD/DP predictions of the present method for excited configurations are compared with Bacher and Goudsmit, F and G parameter method, and Layzer's values and experiment in Table XI. The agreement of our predictions with experiment is seen to be better in all cases except one where the Bacher and Goudsmit prediction is better. The all-external pair correlations used for this calculation are also from the ground-configuration all-external energy data.

VI. CONCLUSION

In the first paper of this series, a theory of electron correlation for the general nonclosed-shell atomic species and methods of evaluation were developed. The theory is applicable to excited configurations and states as well as ground-state species. Three kinds of correlation effects, (1) "internal," (2) "semi-internal and polarization," and (3) "all-external" correlations, were distinguished. The first two were found to be strongly Z, N, and symmetry-dependent. The third effect was very similar to correlations in closed shells[2] and consisted mainly of transferable pair correlations. The internal and semi-internal polarization energies and wave functions were calculated by a CI method for 113 states arising from $1s^22s^n2p^m$ ($n = 0, 1, 2$; $m = 0, 1, 2, \ldots, 6$) configurations of B, C, N, O, F, Ne, and Na atoms and their ions. The all-external energy of each species was then evaluated by subtracting the other two correlation energies from "experimental" total correlations. The numerical results showed that all three effects are important in magnitude and the all-external

TABLE XI. $(SD)/(DP)$ term-splitting ratios.

Configuration	Z	B. G. (Ref. 17)	F and G parameter method[a]	Layzer (Ref. 12)	Present calculation	Observed (Ref. 9)
$1s^22s2p^2$	6	4.34	1.50	1.44	2.75	2.30
	7	3.41	1.50	1.46	2.37	2.09
	8	3.07	1.50	1.47	2.12	1.92
$1s^22s2p^3$	7	1.10	1.50	1.54	0.89	0.95
	8	1.18	1.50	1.53	0.99	1.10
$1s^22s2p^4$	8	1.92	1.50	1.48	2.30	1.94
$1s^22p^2$	7	•••	1.50	2.03	4.44	3.49
	8	•••	1.50	2.03	3.66	3.15

[a] F and G parameter method always yields 1.50 for SD/DP term-splitting ratios.

[b] All-external pair energies used in this calculation were obtained from ground configuration data. These values are therefore actual predictions and not the results of a best fit.

energy is approximately Z-transferable.

In the present paper we have analyzed the all-external correlation energies obtained in I into their irreducible all-external pair components. The extraction of irreducible all-external pair energies from the "experimental" all-external energy data was performed through a least-squares analysis treating the pair energies as unknown constants. The pairs obtained this way were seen to reproduce the all-external energies of many species well within the error limits of the "experimental" all-external energy data. The result confirms the predictions of the MET developed by Sinanoğlu and co-workers[2–5] that "the all-external pair correlations are, to a good approximation, additive and transferable and that once the internal and semi-internal correlations are taken out the remaining correlations consist mainly of these pairs even in highly excited states."

The theory of the first paper and the present one was then used for a method of prediction of atomic energies. The method was applied to predictions of electron affinities, energies of excited states of negative ions, excitation energies, intermultiplet separations, and term-splitting ratios. These predictions involved negative ions and excited states with one or two ($2s$) holes in the original configurations, as well as other singly or doubly excited configurations. The semiempirical "all-external pair-correlation energies" that entered these predictions were obtained from ground configurations of positive ions or neutral atoms. Agreement of the present method with experiment was seen to be better than conventional methods including those which used many empirical parameters obtained from the configurations to be predicted.

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