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THEORY OF ATOMIC STRUCTURE INCLUDING ELECTRON CORRELATION

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We develop a theory of atomic structure treating electron correlation for excited and ground configurations, and apply it to 113 states of the $1s^k2s^n2p^m$ type, in boron through sodium and their ions. Predictions agree better with experiment than the traditional methods.

There are anomalous correlation effects in nonclosed shells, especially in excited configurations and states of atoms, not found in closed shells. This Letter presents an N-body theory of correlation effects for excited states of atoms, applicable also to ground states. The method is applied to 113 species from configurations of the type $1s^22s^n2p^m$ ($n=0,1,2$; $m=0$ to 6). The types of correlation indicated by the theory are evaluated and analyzed. They are used for prediction of energies and related quantities such as electron affinities and term-splitting ratios of excited configurations. Some of the wave functions obtained, which contain important correlation effects, have been used to get properties like transition probabilities. The main features of the theory are outlined here and sample results given. The mathematical formulation and extensive results are omitted.

The F and G parameter methods of Condon and Shortley[1] and Slater[2] are based on orbital theory, though the semiempirical parameters may contain some correlation effects. The Bacher-Goudsmit[3] theory treats total energies without separation of orbital and correlation effects. Configuration interaction (CI) does treat correlation separately if a Hartree-Fock (HF) function is the starting point. However, it deals with the total N-electron wave function, and is applied to each state of each N-electron system as a different problem.

One of us has shown that the HF part of the wave function takes care of most of the long-range part of the Coulomb repulsion and, once this is taken out, the correlation effects result from shorter range "fluctuation potentials" between electrons.[4] For a systematic, more accurate treatment of N-electron systems it is advantageous to deal with correlation effects separately. For closed-shell systems the short range of this potential and the "exclusion" effects studied by perturbation theory[5,6] causes decoupled pair correlations to become dominant. This approach was later generalized into a nonperturbative "many-electron theory of atoms and molecules" (MET).[4] Methods of examining 1-, 3-, 4-, ⋯ -electron correlations as well as the dominant pair correlations were developed. The N-electron correlation problem was reduced to $\frac{1}{2}N(N-1)$ separate two-electron problems.

In nonclosed shells the especially excited configurations and states, other novel correlation effects arise. These will now be analyzed and incorporated into a theory of atomic structure applicable to excited configurations. Nonclosed shell correlation effects were studied first by perturbation theory (Silverstone and Sinanoğlu[7]); the present theory is a nonperturbative one.[8]

The restricted Hartree-Fock (RHF) function developed by Roothaan[9] is the starting orbital wave function.

According to the present theory, nonclosed-shell correlations separate mathematically and physically into three types:

(I) Internal correlations consist of virtual transitions of electrons from filled to vacant orbitals within the HF sea.[10] The main part of this effect occurs in near-degeneracy type CI[11] or equivalently in multiconfigurational self-consistent field (SCF) calculations.[12]

(II) Semi-internal correlations arise from virtual excitations where one electron shifts within the HF sea while the other goes outside.[10] The importance of this effect was first noted in Ref. 11. Some single excitations due to symmetry polarizations are considered together with this effect.[7]

(III) All-external correlations are mainly pairs of electrons going to two-electron functions outside the HF sea.[10]

I and II are unique to open shells and result from (near) degeneracies between the occupied and vacant HF-sea orbitals. They are nondynamical,[11] i.e., strongly Z, N, and symmetry dependent. These can be obtained by a quite small CI calculation. The internal effect in the first row is dominated by the $1s^2 2p^{n+2}$ mixing. The semi-internal effect is also obtainable from a finite CI since the configurations that mix are limited by symmetry and by the fact that one of the two correlating electrons must remain in the HF sea. These two effects were calculated by CI for 113 states of B, C, N, O, F, Ne, and Na atoms and their ions in ground and excited configurations. Virtual $2s$ and $2p$ orbitals of the HF sea were assigned the same radial parts as their occupied counterparts. Single-electron correlation functions for the semi-internal effect were well represented by one Slater-type orbital with and optimized exponent.

The results for the internal energy confirm that this correlation not only increases with Z for a given state[13] but, for ground states, decreases across the first row with a number of $2p$ electrons with parallel spin.[11] For $1s^2 2s^2 2p^n$ configurations the semi-internal correlation is mainly due to $2s2p \rightarrow 2p'F$ excitations where F is the one-electron correlation function above; here it contains at most s, p, d, and f compenents orthogonal to $1s$, $2s$, and $2p$. For $1s^2 2s 2p^n$ and $1s^2 2p^n$, $2p2p' \rightarrow 2sF$ excitations contribute as much or more than $2s2p \rightarrow 2p'F$ types.

The all-external correlation energies can be found by subtracting internal and semi-internal energies from the total "experimental"[14] correlation energies. Some typical results in Table I show the relative magnitudes of the three types of correlation. The semi-internal energy is considerable.

According to MET, once the first two specific effects are taken out, the remaining "all-external" correlation is similar to that in closed shells, which consist mainly of $\frac{1}{2}N(N-1)$ "dynamical" (transferable among systems of different N, symmetry, and to a lesser extent Z) pair correlations.[4,7] Many of these pair correlation energies (between pairs of HF orbitals) are related by symmetry ["$B(ij)$-type" or "reducible" pairs].[6] A second kind of pair correlations, "irreducible pairs," were also introduced,[15] and are related to the first kind by a unitary transformation. The "irreducible pairs," here belonging to irreducible representations of $[\mathrm{O}(3) \otimes \mathrm{SU}(2)\ \mathrm{spin}]$, are convenient for nonclosed-shell states. Each is weighted by its occupation number in the HF sea. Thus from each species calculated we get

Table I. Internal (E_{int}), semi-internal ($E_{s\ \mathrm{int}}$), all external ($E_{\mathrm{all\ ex}}$) correlation energies in some states and ions of nitrogen and oxygen. (Values in eV.)

Configuration	$1s^2 2s^2 2p^2$			$1s^2 2s^2 2p^3$			$1s^2 2s 2p^2$			
state	^3P	^1D	^1S	^4S	^2D	^2P	^4P	^2D	^2S	^2P
$Z=7$ E_{int}	−0.58	−0.56	−2.15	0.00	0.00	−0.95	0.00	0.00	0.00	0.00
$E_{s\ \mathrm{int}}$	−1.14	−1.15	−0.07	−1.28	−1.31	−0.59	−0.14	−1.13	−0.18	−1.60
$E_{\mathrm{all\ ext}}$	−2.83	−3.18	−3.74	−3.84	−4.35	−4.76	−1.97	−2.40	−3.22	−2.54
$Z=8$ E_{int}	−0.68	−0.67	−2.57	0.00	0.00	−1.17	0.00	0.00	0.00	0.00
$E_{s\ \mathrm{int}}$	−1.20	−1.23	−0.05	−1.40	−1.45	−0.64	−0.15	−1.14	−0.14	−1.64
$E_{\mathrm{all\ ext}}$	−2.88	−3.27	−3.80	−3.85	−4.35	−4.76	−2.13	−2.52	−3.28	−2.68

an equation where the all-external energy is expressed in terms of all-external irreducible pair correlation energies. If we have n_p irreducible pairs any linearly independent n_p equations (for a given Z) could yield the pair energies semiempirically. But since we always have more equations than necessary for a unique solution, we performed a least-squares analysis, taking the pair parentage coefficients as the linear variables and the pair energies as the constants sought. Two sets of such analyses were done. In one $1s^22s2p$, $1s^22s2p^2$, and $1s^22s2p^3$ as well as $1s^22s^22p^n$ were used. In the second we used only ground configuration data. For example, the irreducible all-external pair energies in eV for N are as follows[16]: First set (all data): $\epsilon(1s^2) = -1.23$, $\epsilon(1s^22s) = -0.07$ [here and below ϵ's involving three orbitals are actually combinations of two pairs; e.g., $\epsilon(1s^22s) = \frac{3}{2}\epsilon(1s2s;{}^3S) + \frac{1}{2}\epsilon(1s2s;{}^1S)$], $\epsilon(1s^22p) = -0.10$, $\epsilon(2s^2) = -0.15$, $\epsilon(2s2p;{}^3P) = -0.13$, $\epsilon(2s2p;{}^1P) = -0.55$, $\epsilon(2p^2;{}^3P) = -0.20$, $\epsilon(2p^2;{}^1D) = -0.48$, $\epsilon(2p^2;{}^1S) = -1.17$. Second set (only ground configurations): $\epsilon(1s^2) = -1.26$, $\epsilon(1s^2 - 2s) = -0.07$, $\epsilon(1s^2 - 2p) = -0.10$, $\epsilon(2s^2) = -0.15$, $\epsilon(2s2p;{}^3P) = -0.12$, $\epsilon(2s2p;{}^1P) = -0.49$. [$\epsilon(2s^2 - 2p)$ cannot be separated into singlet and triplet components without excited configuration information. The separation here assumes the same ${}^3P/{}^1P$ ratio as in the first set.] $\epsilon(2p^2;{}^3P) = -0.24$, $\epsilon(2p^2;{}^1D) = -0.59$, $\epsilon(2p^2;{}^1S) = -1.17$. Small $\epsilon(2s^2)$ and $\epsilon(1s^2 - 2p)$ values did not enter the analysis directly. Their values from Ref. 11 and Kelly[17] were subtracted from the all-external correlation energy prior to calculation. Also, $\epsilon(1s^2 - 2s)$ of the first set comes from the second set.

The accuracy of the least-squares fit is a measure of the predicted[4] transferability and additivity of all-external pairs. In the first and second sets 10 and 21 data points were used for six unknown pairs. The rms and maximum errors for the two sets are 0.049 and 0.105 eV for the first and 0.021 and 0.047 eV for the second. All these errors are less than the error of "experimental"[14] correlation energies which for N is about 0.25 eV.

The all-external pair energies can reproduce the all-external correlation energies of many states quite accurately. Table II compares some all-external energies calculated from the pairs with "experimental" ones. The agreement is a further demonstration of the all-external pair transferability and additivity predicted by MET.[4]

We can now give a relatively easy method for the prediction of the energy of any atomic species $1s^k2s^n2p^m$. Extension to states involving other orbitals is straightforward. The method is as follows: (a) one gets HF and relativistic energies as explained in Ref. 14; (b) the internal and semi-internal correlation energies are calculat-

Table II. Nitrogen comparison of "experimental all-external" correlation with those calculated from the semiempirical pairs of this paper for excited configurations. (Values in eV.)

Species		$E_{\text{"exp."}}$(all-ext.corr.)[a]	First Set[b]		Second Set[c]	
			Calculated	Error	Calculated	Error
$1s^22s2p$	${}^3P$	-1.57	-1.54	0.03	-1.55	0.02
	${}^1P$	-1.95	-1.95	-0.00	-1.91	0.04
$1s^22s2p^2$	${}^4P$	-1.98	-1.97	0.01	-2.01	-0.04
	${}^2D$	-2.40	-2.46	-0.06	-2.54	-0.14
	${}^2S$	-3.22	-3.15	0.07	-3.12	0.10
	${}^2P$	-2.54	-2.59	-0.05	-2.56	-0.02
$1s^22s2p^3$	${}^5S$	-2.55	-2.60	-0.05	-2.72	-0.17
	${}^3D$	-3.19	-3.23	-0.04	-3.42	-0.23
	${}^3P$	-3.71	-3.69	0.02	-3.80	-0.09
	${}^1D$	-3.58	-3.64	-0.06	-3.79	-0.21
	${}^3S$	-3.48	-3.42	0.05	-3.45	0.02

[a] $E_{\text{"exp"}}$(all-ext corr) $\equiv E_{\text{corr}}(\text{"exp"}) - E_{s-\text{int}+\text{int}}$; for E_{corr}("exp") see Ref. 14.

[b] Pairs from all available data (see text).

[c] Pairs from ground configurations only (since the configurations reported in this table were not used in this set, these values constitute true predictions).

Table III. Comparison of electron affinities and term splitting ratios predicted by this theory with experimental values and predictions of other theories.

	Electron affinities (eV)				(*SD*/*DP*) splitting ratios				
Atom	TC[a]	HF[b]	Obs[c]		TC[a]	Obs[d]	Layzer[e]	BG[f]	*F* & *G* method[g]
C	1.17	0.55	1.25	$1s^22sp^2$ $Z=7$	2.37	2.09	1.46	3.41	1.50
N	−0.45	−2.15	···	$Z=8$	2.12	1.92	1.47	3.07	1.50
O	1.24	−0.54	1.465	$1s^22p^2$ $Z=7$	4.44	3.49	2.03	···	1.50
F	3.23	1.36	3.448	$Z=8$	3.66	3.15	2.03	···	1.50

[a] This calculation. All-external correlation energies used in these calculations are from the second irreducible pair set (see text). No data involving the species in this table was used in this set; therefore these values are true predictions and not the result of a best fit.

[b] From E_{RHF} values of the references given in Ref. 9 of text.

[c] Observed electron affinities [B. L. Moiseiwitsch, Advan. Atomic Mol. Phys. 1, 61 (1965)].

[d] Observed term-splitting ratios obtained from Moore (see Ref. 14).

[e] From D. Layzer, Ann. Phys. (N.Y.) 271 (1959).

[f] Obtained from Ref. 3.

[g] *F* and *G* parameter method (Ref. 2, Chap. 13-15).

ed by CI; (c) the all-external energy is obtained using pair values given here and in forthcoming papers. The total energy of the species is found by summing (a), (b), and (c). Some predictions of electron affinities and term-splitting ratios for excited configurations are given in Table III, with experimental values and predictions of other nonextrapolative theories. The present method works better than traditional techniques, as the comparison shows.

The internal and semi-internal wave functions obtained from (b) above, with the HF function, contain all the specific parts of the wave function. The rest is expected (though this is unproven) to change the charge density little. The above functions have been used to calculate transition probabilities.[18]

These methods may be extended to higher rows. However in these cases the estimates of relativistic energies become unreliable. Therefore a relativistic HF wave function would be a desirable starting point. A study of these extensions is in progress.

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[10] For the first row the HF sea contains the $1s$, $2s$, $2p$ orbitals. If a pair function $\hat{u}_{ij}'$ is "outside" the sea then $\langle \hat{u}_{ij}' \,|\, k\rangle_{\vec{x}_i} = \int \hat{u}_{ij}(\vec{x}_i, \vec{x}_j) k^*(\vec{x}_i) d\vec{x}_i = 0$, where k is any orbital of the sea.

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[14] $E_{\mathrm{corr}}(\text{"exp"}) = E_{\mathrm{total}} - E_{\mathrm{RHF}} - E_{\mathrm{rel}}$. E_{RHF} is obtained by the methods of Ref. 9; these values must be corrected for finite nuclear mass. We estimated E_{rel} from C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. 127, 830 (1962). E_{total} is from C. Moore, Atomic Energy Levels, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office,

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[16] Parts of the internal and semi-internal energies consist of pair excitations. The sum of internal, semi-internal, and all-external contributions coming from a given pair are defined as the total pair correlation energy. Pair correlations studied in Ref. 11 are of this "total" type. For example the $e(2s^2)$ and $\epsilon(2s^2 \to 2p)$ total correlations for N^+ $1s^2 2s^2 2p^2 (^3P)$ are −0.73 and −1.53 ev, while the "all-external pair energies" are −0.15 and −0.47 ev.

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NUCLEAR SPIN-LATTICE RELAXATION VIA PARAMAGNETIC CENTERS WITHOUT SPIN DIFFUSION*

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Experiments have been performed which study the relaxation of a nuclear spin system by paramagnetic impurities under conditions which inhibit spin diffusion. When spin diffusion is effectively absent, the magnetization is found ultimately to approach its equilibrium value as $\exp[-(t/\tau_1)^{1/2}]$. An expression is obtained describing the relaxation of such a diffusionless spin system valid for all times and in agreement with experiment. Under suitable conditions higher order spin diffusion effects are also observed.

Blumberg[1] has proposed that a diffusionless spin system relaxed by paramagnetic impurities and characterized by a small critical radius ρ_c should initially relax as $1-(t/\tau_1)^{1/2}$, and experiments support this result.[1,2] We have found that a diffusionless spin system ultimately relaxes as $\exp[-(t/\tau_1)^{1/2}]$, which is in agreement with a theory valid for all times and reduces to Blumberg's result when $\rho_c \to 0$.

Our measurements were made using a CaF_2 crystal containing 0.06 mole% EuF_3 in CaF_2. In all cases the [111] direction was oriented along a static applied magnetic field H_0 of 6600 G, and the CaF_2 crystal was immersed in liquid nitrogen. The spin-lattice relaxation time T_1 of the fluoride nuclei in the high field H_0 was 432 msec.

When the F^{19} spin system is prepared so that its magnetization is directed along an intense, circularly polarized, resonant magnetic field $\vec{H}_1$, the magnetization is spin locked[3] along $\vec{H}_1$ and is depolarized by the noise fields of the paramagnetic impurities. We find that after about 50 μsec, the magnetization can be approximated by an expression $M_0(\alpha-\beta t^{1/2})$ until it assumes its typical $\exp(-t/T_1^r)$ behavior with a T_1^r of 4.4 msec. The $M_0(\alpha-\beta t^{1/2})$ behavior had been misinterpreted earlier[4] as an example of Blumberg's result[1] in that the constant α was set equal to unity. Our measurements indicate that for very short times there is a serious departure from the $M_0(\alpha-\beta t^{1/2})$ behavior and that the linear dependence on $t^{1/2}$ is somewhat spurious. The experimental results of Blumberg also yield better agreement with $1-(t/\tau_1)^{1/2}$ behavior than is warranted by the correct $\exp[-(t/\tau_1)^{1/2}]$ expression and this can be explained by the onset of spin diffusion.

In order to perform a relaxation measurement with a minimum of spin diffusion, the F^{19} spin system is prepared by polarizing it along a nonresonant, circularly polarized field

$$\vec{H}_{\rm eff} = H_1 \cos\omega t\,\hat{x} + H_1 \sin\omega t\,\hat{y} + (H_0 - \omega/\gamma)\hat{z}, \tag{1}$$

which is chosen so that the most effective spin-spin interaction terms in the rotating frame disappear. If we write the Hamiltonian of the F^{19} spin system as

$$\mathcal{H} = \hbar\omega_0 I_z + \hbar\omega_1 (I_x \cos\omega t + I_y \sin\omega t) + \sum_{j,k}{}' \gamma^2\hbar^2 r_{jk}^{-3}(3\cos^2\theta_{jk} - 1)(\vec{I}_j\cdot\vec{I}_k - 3I_{zj}I_{zk}), \tag{2}$$

where $I_\alpha = \Sigma_j I_{\alpha j}$, $\vec{r}_{jk}$ is the vector between F^{19} sites j and k, ω is the angular frequency of the rf field, and θ_{jk} is the angle between the z axis and $\vec{r}_{jk}$, then the transformation

$$\rho = \exp(-i\varphi I_y - i\omega I_z t)\rho^* \exp(i\omega I_z t + i\varphi I_y) \tag{3}$$