



Many-Electron Theory of Atoms and Molecules. V. First-Row Atoms and Their Ions

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Many-Electron Theory of Atoms and Molecules. V. First-Row Atoms and Their Ions*†

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The correlation energies of the $1s^2 2s^2$ inner cores of the first-row atoms B, C, ..., Ne are found to be very different from those of the corresponding four-electron Be-like ions, B^+ to Ne^{6+} , due to the exclusion effects of the outer $2p$ electrons. Whereas the $2s^2$ correlation, $\epsilon(2s^2)$, in the $1s^2 2s^2$ ions increases from -1.13 eV in Be to -3.2 eV in Ne^{6+} , the $2s^2$ correlation in the neutral atoms decreases from -1.13 eV in Be to -0.27 eV in Ne. The many-electron theory was used for the nonempirical $2s^2$ calculations and included the use of the r_{12} coordinate. With these theoretical $\epsilon(2s^2)$ values the correlation of a $2p$ electron with the $1s^2 2s^2$ inner core is found to be large, ~ -1 eV. Also the $2p^2$ correlation comes out about -1 eV. The results show that core energies will, in general, depend strongly on the state and number of the outer-shell electrons and that intershell correlation interactions may be appreciable. Implications for π -electron systems and the ligand-field theory of inorganic complexes are discussed.

INTRODUCTION

THIS series of papers has been developing a theory of many-electron atoms and molecules including electron correlation effects.¹ Paper I systematically analyzed the correlation effects in the wavefunction and energy of a many-electron system showing the pair correlations to be by far the most important. Paper II developed methods for obtaining the pair correlations. Paper III obtains the effect of correlation on orbitals and shows them to be negligible on the Hartree-Fock part of the wavefunction. In Paper IV nonempirical calculations are carried out on the Be atom and its ions. The changes in Be^{2+} ion when it is turned into the core of Be^{1+} or Be are obtained quantitatively studying the usual "neglect" of the $1s^2$ -type inner shells. The $1s^2$ pair correlation in Be, $\epsilon(1s^2)$, differs very little from $\epsilon(1s^2)$ in Be^{2+} or Be^+ . Such pair correlations are transferable. This "inner-shell" cancellation is basic to much of quantum chemistry.

Paper V gives a theoretical analysis of the changes of correlation energies in the ground states of the first-row atoms and their ions. This includes changes both with the total number of electrons N , and the nuclear charge Z . The $1s^2$ core of Be is very much like the $1s^2$ electrons in Be^{2+} or Be^+ (Paper IV). Comparing Be^+ and Be we can "cancel" out such inner cores,²

$\epsilon(1s^2)$. But how far can we go with such "inner-shell cancellations?" Is the $1s^2 2s^2$ core of carbon the same as $1s^2 2s^2$ of C^{2+} ? Can we put the $1s^2 2s^2 F^{6+}$ ion into a F atom? Our results show that the answer is no. These cores, the $2s^2$ part, change drastically when we put $2p$ electrons on top of them.² The $\epsilon(2s^2)$ will be calculated nonempirically using the many-electron theory. $\epsilon(2s^2)$ drops from -1.13 eV in Be to almost zero³ in nitrogen through to Ne (see Paper I). Contrary to previous empirical results,⁴ which show $\epsilon(2s^2)$ increasing from -1.03 eV in Be to -3.2 eV in Ne, these new $\epsilon(2s^2)$ show that $\epsilon(2p \rightarrow 1s^2 2s^2)$, the correlation of a $2p$ electron with the $1s^2 2s^2$ core of the atom, is large ~ -1.0 eV. Previous results⁴ gave $\epsilon(2p \rightarrow 1s^2 2s^2) \approx -0.25$ eV. Also $\epsilon(2p^2)$ is about -1.0 eV and not -1.72 eV.⁴

"EXPERIMENTAL" CORRELATION ENERGIES OF ATOMS AND THEIR IONS

From total experimental energies, Hartree-Fock (HF) energies (E_{HF}) and relativistic estimates (accurate to within 5%),⁴ Clementi⁴ has obtained the correlation energies of atoms and ions of the first row (see also Fig. 1). His graphs⁴ show the change in total $E_{corr.}$ with N number of electrons, and Z nuclear charge [see also Ref. 3(b) for some detailed graphs]. These graphs bring out three main features: (a) In the Be-like ions, Be, $B^+ \dots Ne^{6+}$, the total correlation energy increases linearly with Z . The $2s^2$ correlation increases with Z , not $\epsilon(1s^2)$. Linderberg and Shull⁵ predicted this Z dependence from $2s$ - $2p$ degeneracy in the limit of infinite Z . (b) When one $2p$ electron is added,

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¹ Papers are referred to as follows: (I) O. Sinanoğlu (pair versus many-electron correlations), *J. Chem. Phys.* **36**, 706 (1962); (II) O. Sinanoğlu (methods for pair correlations), *J. Chem. Phys.* **36**, 3198 (1963); (III) O. Sinanoğlu and D. F. Tuan (effect of correlation or orbitals, f_i 's), *J. Chem. Phys.* **38**, 1740 (1963); (IV) D. F. Tuan and O. Sinanoğlu (Be^{2+} , Be^+ , and Be), *J. Chem. Phys.* **41**, 2677 (1964).

² This paper deals only with changes in the correlation part of a pair of electrons. Changes in the Hartree-Fock part are well understood.

³ See (a) O. Sinanoğlu, *Proc. Natl. Acad. Sci. (U.S.)* **47**, 1217 (1961) (b) O. Sinanoğlu, *Advan. Chem. Phys.* **6**, 315-412 (1964).

⁴ E. Clementi, *J. Chem. Phys.* **38**, 2248 (1963); see also L. C. Allen, E. Clementi, and H. M. Gladney, *Rev. Mod. Phys.* **34**, 465 (1963).

⁵ J. Linderberg and H. Shull, *J. Mol. Spectry.* **5**, 1 (1960).

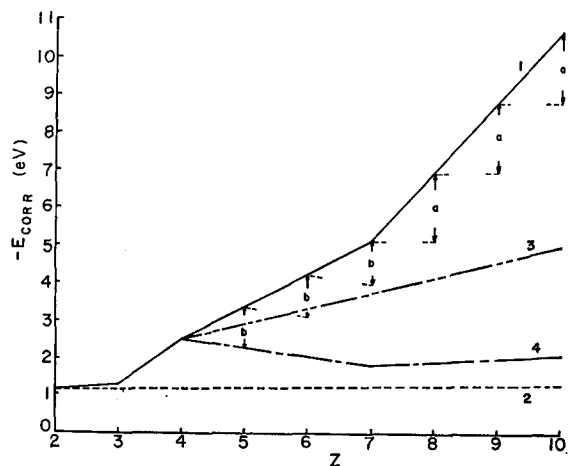


FIG. 1. Correlation energy of first-row atoms and their ions. Curve 1: Total "experimental" correlation energy of the ground states of first-row atoms (Ref. 4). Curve 2: Total correlation energy of He-like ions (Ref. 4). Curve 3: Correlation energy of four-electron $1s^2 2s^2$ ions (Ref. 4). Curve 4: Correlation energy of $1s^2 2s^2$ inner cores in neutral atoms (obtained by adding the calculated $\epsilon(2s^2)$ [see text] to the semiempirical $\epsilon(1s^2)$ and $1s-2s$ intershell correlations [see Paper IV¹]. Segment *a* is the $2p^2$ correlation plus the correlation of a $2p$ electron with the $1s^2 2s^2$ core (see text). Segment *b* is the correlation energy of one $2p$ electron with the $1s^2 2s^2$ core (see text).

turning Be-like ions into B-like ions: total correlation energy increases by -0.35 eV in B and -0.16 eV in Ne^{5+} . Total E_{corr} still increases with Z and almost parallel to the Be-like ions. (c) There is an increase of about -1.7 eV as soon as $2p$ electrons pair up, e.g., ($2p_0\alpha 2p_0\beta$). We expect such an increase.

The small increase in total E_{corr} on adding a $2p$ electron, (b) above, naturally leads to two empirical conclusions⁴: (i) This very small increase in total E_{corr} is the correlation of a $2p$ electron with the inner $1s^2 2s^2$ core; (ii) the inner core, $1s^2 2s^2$, has pretty much the same correlation as the $1s^2 2s^2$ of the free four-electron ion.

But $2s^2$ correlation is a near-degeneracy-type correlation ("nondynamical"),^{3b,5} very different from $1s^2$ correlation ("dynamical"). The many-electron theory shows that these "nondynamical" pairs, in contrast to "dynamical" pairs, are very sensitive to the rest of the Hartree-Fock "sea." The total Hartree-Fock potential influences the pair of electrons ("immersion effects") and also while correlating in this sea a "nondynamical" pair is strongly prevented from making excitations to other occupied orbitals⁶ ("exclusion" effects).

On this basis we expect the $2s^2$ correlation to decrease from -1.13 eV in Be to about zero in nitrogen and remain about zero all the way up to neon.^{3b} What is the source of the apparent contradiction between

⁶ O. Sinanoğlu, J. Chem. Phys. **33**, 1212 (1960); see also O. Sinanoğlu, Proc. Roy. Soc. (London) **A260**, 379 (1961).

the empirical $2s^2$ and $2s-2p$ correlation picture and these theoretical predictions? There are three possible reasons: (a) "Dynamical" correlation may be increasing in $\epsilon(2s^2)$ of B, C, etc., even though it is negligible in Be. (b) Perhaps the relativistic corrections are wrong. This is unlikely. (c) $2s-2p$ correlations are large, so that they actually compensate for the decrease in the $2s^2$ correlations and then total E_{corr} 's seem just slightly increased upon the addition of $2p$ electrons.

In the following sections we make detailed calculations with the many-electron theory (a) to get the correct nondynamical effects as influenced by the other electrons and the nuclear charge, (b) to see if dynamical correlation in $2s^2$ subshells remains as small as it is in Be, and (c) to get the correct values for other pair correlations, e.g., $\epsilon(2p \rightarrow 1s^2 2s^2)$. The results resolve the discrepancy and show that the third alternative (c), mentioned above, is the one that correctly accounts for the total E_{corr} trends.

THEORY

All our results are for ground-state atoms of the first row. All are closed-shell systems or have single-determinant Hartree-Fock wavefunctions. For such single-determinant states the total wavefunction^{1,3b} ψ is

$$\psi \cong \phi_0 + \chi_s', \quad (1)$$

with ϕ_0 the HF wavefunction and χ_s' the correlation part so that $\langle \phi_0, \chi_s' \rangle = 0$. For ϕ_0 we use Roothaan's SCF orbitals.⁷ χ_s' is

$$\chi_s' = \mathcal{A} \left\{ (1 \ 2 \ 3 \ \dots \ N) \left[\frac{1}{\sqrt{2}} \sum_{i>j} \frac{\hat{u}_{ij}}{(ij)} + \frac{1}{2} \sum_{i>j} \sum_{k>l} \frac{\hat{u}_{ij}\hat{u}_{kl}}{(ijkl)} + \dots \right] \right\}, \quad i, j \neq k, l. \quad (2)$$

The second and higher terms in Eq. (2) are unlinked clusters [see Eq. (77) of Ref. 3b]. \mathcal{A} is the N -electron antisymmetrizer, $1, 2, \dots, i, j$ are HF spin orbitals and \hat{u}_{ij} 's are pair functions. Closed shell \hat{f}_i 's are about zero (Paper III).^{1,3b} Nonclosed-shell \hat{f}_i 's here are also very small because we have single determinant HF ϕ_0 's.^{3b} With the very small \hat{f}_i effects neglected (estimates given in Paper III),¹ the total energy E of the many-electron atom becomes^{3b}

$$E \ll E'_s \equiv E_{\text{HF}} + \sum_{i>j} \epsilon'_{ij} + \frac{R'}{D'} \quad (3)$$

with

$$D' = 1 + \langle \chi_s', \chi_s' \rangle. \quad (4)$$

⁷ C. C. J. Roothaan and P. S. Bagus in *Methods in Computational Physics* (Academic Press, Inc., New York, 1963), Vol. 2, p. 47.

$\bar{\epsilon}'_{ij}$ is the pair correlation energy and R' the three or more Coulomb correlations.

$$\bar{\epsilon}'_{ij} \approx \frac{2\langle \mathcal{B}(ij), m_{ij}\hat{u}_{ij} \rangle + \langle \hat{u}_{ij}, (e_i + e_j + m_{ij})\hat{u}_{ij} \rangle}{1 + \langle \hat{u}_{ij}, \hat{u}_{ij} \rangle}, \quad (5)$$

\mathcal{B} is the two-electron antisymmetrizer.

$$m_{ij} = (r_{ij})^{-1} - \bar{S}_{ij} + \bar{J}_{ij}, \quad (6)$$

$$\bar{S}_{ij} = \bar{S}_i(\mathbf{x}_j) + \bar{S}_j(\mathbf{x}_i). \quad (7)$$

The self-potentials $\bar{S}_i(\mathbf{x}_i)$ should be included in \bar{S}_{ij} , e_i , and m_{ij} . They are not shown in Eq. (7) since in the exact pair expressions ϵ_{ij} these self-potentials cancel out. $\bar{S}_j(\mathbf{x}_i)$ is the Coulomb plus exchange potential of spin-orbital j acting on i , i.e.,

$$\bar{S}_j(\mathbf{x}_i) i(\mathbf{x}_i) = \langle j(\mathbf{x}_j), (r_{ij})^{-1} j(\mathbf{x}_j) \rangle_{\mathbf{x}_j} i(\mathbf{x}_i) - \langle j(\mathbf{x}_j), (r_{ij})^{-1} i(\mathbf{x}_j) \rangle_{\mathbf{x}_j} j(\mathbf{x}_i), \quad (8)$$

$$\bar{J}_{ij} = J_{ij} - K''_{ij}. \quad (9)$$

J_{ij} and K''_{ij} are Coulomb and exchange integrals. e_i is

$$e_i \equiv h_i^0 + V_i(\mathbf{x}_i) - \epsilon_i. \quad (10)$$

ϵ_i is the HF orbital energy of i and V_i the total HF potential acting on spin-orbital i . h_i^0 is the bare nuclei Hamiltonian. For details see Paper I and Ref 3(b). \hat{u}_{ij} is orthogonal to all occupied HF spin-orbitals ("exclusion" effect), i.e.,

$$\langle \hat{u}_{ij}, k(\mathbf{x}_i) \rangle_{\mathbf{x}_i} = 0. \quad (11)$$

The pair energy $\bar{\epsilon}'_{ij}$, Eq. (5), is for a closed-shell single-determinant HF. For single-determinant non-closed-shell HF $\bar{\epsilon}'_{ij}$ must be re-examined because the total HF potential V_i acting on each electron is different. We do this in Appendix A and the new $\bar{\epsilon}'_{ij}$ has almost the same form as Eq. (5). From Eq. (5), pairs can now be calculated one by one just like the helium-type atom. But Eq. (5) contains the total Hartree-Fock potential in $V_i(\mathbf{x}_i)$ ["immersion" effects Eq. (10)], and the exclusion effect [Eq. (11)], keeping a \hat{u}_{ij} orthogonal to occupied HF orbitals.

To use Eq. (5) we start from any two-electron function $\psi_{ij}(\mathbf{x}_i, \mathbf{x}_j)$. To fit this into the many-electron theory ψ_{ij} is written as

$$\psi'_{ij} = \mathcal{B}(ij) + u_{ij}^0 \quad (12)$$

and

$$\langle \mathcal{B}(ij), u_{ij}^0 \rangle = 0 \quad (13)$$

by a change of normalization. The projection operator Q (see Paper II)

$$Q = 1 - (2)^{\dagger} \sum_{k \geq 1}^N \mathcal{B}\{k\} \langle k \rangle + \sum_{l > k \geq 1}^N \mathcal{B}(kl) \langle \mathcal{B}(kl) \rangle \quad (14)$$

then turns u_{ij}^0 into \hat{u}_{ij} . \hat{u}_{ij} can contain r_{ij} or be of the CI type, etc.

These pair functions also give R' , Eq. (3), but this is small.^{3b}

CALCULATION OF $2s^2$ CORRELATIONS (NONDYNAMICAL)

In this section we use a "near-degeneracy" type \hat{u}_{ij} to get $2s^2$ correlation in Be, B, C, ..., Ne. For Be

$$\hat{u}_{34} = c(\mathcal{B}(2p_{+1}\alpha 2p_{-1}\beta) - \mathcal{B}(2p_{+1}\beta 2p_{-1}\alpha) - \mathcal{B}(2p_0\alpha 2p_0\beta)). \quad (15)$$

This gives almost all of the $\epsilon(2s^2)$ in Be (Table I; see also Paper IV¹) and Be-like ions (Table II). The "virtual" $2p$ functions used in these calculations [\hat{u}_{34} , Eq. (15)] were obtained from the $1s^2 2p^2 ({}^1S)$ states using Roothaan's Hartree-Fock programs⁷ (two STO's per $2p$).

In boron

$$\phi_0 = \mathcal{A}(1s\alpha 1s\beta 2s\alpha 2s\beta 2p_0\alpha)$$

and

$$\langle \hat{u}_{34}, 2p_0\alpha \rangle = 0. \quad (16)$$

$2p_0\alpha$ is an occupied HF orbital; this exclusion effect,³ Eq. (16), eliminates the $2p_0$ term of \hat{u}_{34} of B⁺, Eq. (15), and makes the nondynamical \hat{u}_{34} in boron:

$$\hat{u}_{34}(\text{boron}) = c_1[\mathcal{B}(2p_{+1}\alpha 2p_{-1}\beta) - \mathcal{B}(2p_{+1}\beta 2p_{-1}\alpha)]. \quad (17)$$

Adding another $2p$ electron gives, in the 3P term of carbon,

$$\hat{u}_{34}(\text{carbon}) = c_2 \mathcal{B}(2p_0\alpha 2p_0\beta). \quad (18)$$

In Eqs. (16) to (18) it is assumed that the "virtual" $2p$ orbitals taken in the \hat{u}_{34} functions are the same as the *actual* occupied $2p$ orbitals that occur in the ground state ϕ_0 's. We calculated these nondynamical $\epsilon(2s^2)$'s in boronlike and carbonlike ions with such $2p$ orbitals. All the HF orbitals were generated with Roothaan's programs. The basis set was two STO's per $2p$ HF orbital and three STO's for each $2s$ or $1s$ (the $\bar{\epsilon}'_{34}$ is insensitive to the size of the orbital basis set; e.g., in Be going from a three-STO basis to a six-STO basis changes the $\bar{\epsilon}'_{34}$ only by ~ 0.01 eV; see Paper IV¹).

In N(4S), O(3P), F, and Ne \hat{u}_{34} (nondyn) = 0 rigorously⁸ if the $2p$ function in \hat{u}_{34} (nondyn) is the $2p$ orbital of the ground state of each atom (Paper I, p. 714).¹

⁸ Nondynamical correlation remains in N(2P), $\epsilon(2s^2) \approx -0.94$ eV; O(1S), $\epsilon(2s) \approx -1.44$ eV; also $\epsilon(2s^2)$ in 1S of carbon = -1.88 eV, 4 times larger than nondynamical correlation in carbon 3P .

TABLE I. $2s^2$ correlation, $\epsilon(2s^2)$, in first-row atoms (electron volts).

Atom	Empirical ^a $\epsilon(2s^2)$ assuming transferability of ion cores (no exclusion effect)	Theoretical $\epsilon(2s^2)$ ^b (nondynamical with exclusion effect)	Theoretical $\epsilon(2s^2)$ with dynamical (r_{12}) and exclusion effects ^c
Be	-1.034 ^a	-1.132	-0.892
B	-1.387	-0.811	-0.702
C	-1.741	-0.457	-0.408
N	-2.149	-0.0	-0.166
O	-2.421	-0.0	...
F	-2.829	-0.0	...
Ne	-3.155	-0.014 ^d	-0.272

^a L. C. Allen, E. Clementi, and H. M. Gladney, Rev. Mod. Phys. 35, 465 (1963).

^b This work. Calculations based on many electron theory. "Nondynamical" refers to "near-degeneracy" type, here $2s^2-2p^2$ mixing.

^c This work. Pair functions containing r_{12} to include the "dynamical" (slowly convergent with CI) part of the correlation. Calculations include all the orbital orthogonalizations (exclusion effects, etc.) according to the many-electron theory.

^d See text.

Tables I and II give these calculated nondynamical ϵ'_{34} 's for the ground states of Be-like, B-like, and C-like ions ($Z \leq 10$) and those of the neutral atoms Be to Ne. The \hat{u}_{34} (nondyn) in $N(^4S)$, $O(^3P)$, F, and Ne will not be rigorously zero if the virtual $2p$ function of \hat{u}_{34} (nondyn) is different from the $2p$ orbital of the neutral atom. The \hat{u}_{34} can contain any $2p$ function to start with but must then be orthogonalized to the $2p$ orbitals occupied in ϕ_0 of the atom according to Eqs. (11) and (14). This will then reduce such a \hat{u}_{34} (nondyn) to almost zero. For example, a Roothaan HF $2p$ function taken from the $1s^22p^2(^1S)$ state of Ne^{6+} gives a nondynamical $2s^2$ correlation of only -0.014 eV (Table I) when used in the \hat{u}_{34} of 1S Ne atom but -3.25 eV for $2s^2$ correlation in the ground state of Ne^{6+} . Thus the use of the occupied $2p$ orbitals in calculating the nondynamical $\hat{u}(2s^2)$ is justified.

Table I also shows the empirical⁴ $\epsilon(2s^2)$ in these atoms. These are values carried over from the Be-like ion $2s^2$ correlation and assumed unchanged in the neutral atoms.⁴ The empirical and the nonempirical $\epsilon(2s^2)$ have very different trends. But these nonempirical $\hat{u}(2s^2)$ are only nondynamical. Is the dynamical part of $\epsilon(2s^2)$ in B, C, ..., Ne becoming large enough to account for these different trends? We investigate this in the next section.

CALCULATION OF $2s^2$ CORRELATION WITH r_{12} (DYNAMICAL EFFECTS)

In this section we get total $2s^2$ correlation, dynamical plus nondynamical, with a pair function containing r_{12} . The two-electron trial function ψ_{34} is

$$\psi_{34} = \mathcal{B}[2s(3)\alpha(3)2s(4)\mathcal{B}(4)](1 + \gamma r_{34}); \quad (19)$$

γ is a variational parameter. From Eq. (12)

$$u_{34}^0 = c^{-1} \psi_{34}(\mathbf{x}_3, \mathbf{x}_4) - \mathcal{B}[2s(3)\alpha(3)2s(4)\beta(4)], \quad (20)$$

$$c = \langle \psi_{34}, \mathcal{B}[2s(3)\alpha(3)2s(4)\beta(4)] \rangle. \quad (21)$$

The projection operator, Q , of Eq. (14) turns u_{34}^0 into \hat{u}_{34} . This \hat{u}_{34} is not difficult to handle. All integrals were done on an IBM 709 (see Appendix B for details).

Table I gives the $\epsilon(2s^2)$ from these pair functions. $2s^2$ correlation decreases from -0.892 eV in Be to -0.166 eV in N and increases slightly to -0.27 eV in Ne. Optimized values of the variational parameter γ , Eq. (19), are: 0.974(Be), 0.506(B), 0.313[C(3P)], 0.207[N(4S)], 0.414(Ne). Thus we find that the dynamical correlation indeed remains small. The trend in $\epsilon(2s^2)$ we found above with the nondynamical pair functions is real. From an analysis of the correlation energies of Ne $2s$ hole and $2p$ hole states Kestner⁹ finds that in ground state neon $\epsilon(2s^2) < -0.5$ eV, in good agreement with these results.

It must be pointed out that our r_{12} calculations were not made to get really accurate results but just to see if the total $\epsilon(2s^2)$'s show the same trend as the nondynamical $\epsilon(2s^2)$. Had our purpose been to get very accurate results we would have included more terms, e.g., $b(r_1 + r_2)$ terms to help scale our results.¹⁰

OTHER PAIRS

With these nonempirical $\epsilon(2s^2)$ above, we can get the other "dynamical" and quite "transferable" (Paper IV) ϵ_{ij} 's semiempirically from the data. These again are very different from the empirical⁴ ones.

In IV, $\epsilon(1s^2)$ and $1s^2 \rightarrow 2s^2$ intershell correlations were discussed and analyzed, and correct values for the $1s2s$ pairs were obtained for $Z=3$ to 10. Two important pairs still remain for first row atoms: (i) $\epsilon(2p \rightarrow 1s^2 2s^2)$, correlation of a $2p$ electron with the $1s^2 2s^2$ core; (ii) $\epsilon(2p^2)$, tight pair $2p$ correlation. Table III gives $\epsilon(2p^n \rightarrow 1s^2 2s^2) + \epsilon(2p^n)$ i.e., the correlation of n $2p$ electrons with the $1s^2 2s^2$ core and among themselves. This is what is left after the correlation energies of the $1s^2 2s^2$ cores, i.e., the ones in the N -electron "medium" with the proper immersion and exclusion effects calculated above, are subtracted from the total E_{corr} . These new $\epsilon(2p^n \rightarrow 1s^2 2s^2) + \epsilon(2p^n)$ are much larger than the previous non-theoretical ones. Below we obtain the $\epsilon(2p \rightarrow 1s^2 2s^2)$ and the $\epsilon(2p^2)$ parts of these values separately.

⁹ N. R. Kestner, J. Chem. Phys., "2s and 2p Hole States of Ne" (to be published).

¹⁰ For a discussion of scaling see P.-O. Löwdin, J. Mol. Spectry. 3, 46 (1959); M. Veselov, M. Petrashen, and A. Krichaniga [Zh. Eksperim. i Teor. Fiz. 10, 857 (1940)] included such a term, i.e., $b(r_1 + r_2)$ along with αr_{12} to put in correlation between the $2s$ electrons in Be. They used an equation derived by V. Fock et al. [Zh. Eksperim. i Teor. Fiz. 10, 723 (1940)] and obtained a total energy 0.045 a.u. lower than their H.F. energy 14.529 a.u.

TABLE II. $\epsilon(2s^2)$ in Be, B, C (3P) isoelectronic series. Nondynamical (near-degeneracy) correlation here from $2p^4$ mixing [Z is nuclear charge; N is number of electrons (electron volts)].

$Z \backslash N$	4	5	6	7	8	9	10
4	-1.132 ^a	-1.417	-1.828	-2.309	-2.554	-2.900	-3.248
5		-0.811	-1.069	-1.270	-1.477	-1.692	-1.882
6			-0.457	-0.563	-0.656	-0.745	-0.832

^a See Paper IV of this series for $2p$ function used in Be calculation, all other $2p$ functions from HF of ($1s^2 2p^n$) states (see text).

a. $\epsilon(2p \rightarrow 1s^2 2s^2)$

In $C(^3P)$ and $N(^4S)$ all $2p$ electrons have parallel spins. $\epsilon(2p^n)$ is then small [Ref. 3(b) and Paper I]. Most of $\epsilon(2p^n) + \epsilon(2p^n \rightarrow 1s^2 2s^2)$ (Table III) is really $\epsilon(2p^n \rightarrow 1s^2 2s^2)$. From Table III $\epsilon(2p \rightarrow 1s^2 2s^2)$ is ~ 1 eV and $\epsilon(2p^n \rightarrow 1s^2 2s^2)$ is in the ratio 1:2:3 for $n=1, 2, 3$ in B, C, and N, respectively. $\epsilon(2s^2)$ is very different in B, C, and N so the total $E_{\text{corr.}}$ behavior which led to the previous⁴ fortuitous conclusion that $\epsilon(2p \rightarrow 1s^2 2s^2)$ is small ≈ -0.25 eV (also decreasing with Z in boron-like ions)⁴ is accounted for by the actually large $2s-2p$ correlations. As expected total $2s-2p$ correlation is proportional to the number of $2p$ electrons. More results below support this estimate of $\epsilon(2p \rightarrow 1s^2 2s^2) = -1$ eV.

These large values of $\epsilon(2p \rightarrow 1s^2 2s^2)$ are also in line with: (a) From CI Donath¹¹ gives -1.35 to -2.72 eV for the total of six $\epsilon(2p \rightarrow 1s^2 2s^2)$ in F^- , Ne, Na^+ . This gives an $\epsilon(2p \rightarrow 1s^2 2s^2) \approx -0.35$ eV in Ne, already twice the previous estimate⁴ ≈ -0.16 eV. This is only with two configurations for $2s-2p$ correlation. Because of the slow convergence of CI the final $\epsilon(2p \rightarrow 1s^2 2s^2)$ should be at least twice Donath's value. (b) The large $2s-2p$ radial overlap is

$$\int R_{2s} R_{2p} r^2 dr \approx 0.92.$$

The $2s-2p$ correlation is not an "intershell effect" like $\epsilon(1s-2s)$.

TABLE III. $\epsilon(2p^n) + \epsilon(2p^n \rightarrow 1s^2 2s^2)$ in first-row atoms and ions (eV), i.e., the correlation energy of n $2p$ electrons among themselves, $\epsilon(2p^n)$, and with the $1s^2 2s^2$ core, $\epsilon(2p^n \rightarrow 1s^2 2s^2)$. (n is the number of $2p$ electrons; Z is the nuclear charge.)

$Z \backslash n$	5	6	7	8	9	10
1 ^a	-1.137	-1.232	-1.333	-1.411	-1.491	-1.602
1 ^b	-0.354	-0.326	-0.272	-0.245	-0.190	-0.165
2 ^a		-2.317	-2.477	-2.586	-2.737	-2.897
3 ^a			-3.449	-3.533	-3.631	-3.754

^a This work. Using the strong changes in $1s^2 2s^2$ ion cores due to exclusion effects on $\epsilon(2s^2)$.

^b Based on the assumption that $1s^2 2s^2$ ions remain the same in the neutral atoms [L. C. Allen, E. Clementi, and H. M. Gladney, *Revs. Mod. Phys.* **35**, 465 (1963)].

¹¹ W. Donath, *Rev. Mod. Phys.* **35**, 490 (1963). This follows comment by O. Sinanoğlu in Discussion [*Rev. Mod. Phys.* **35**, 489 (1963)] where this problem with $2s^2$ correlation and discrepancies is pointed out. See also Ref. 3(b) and Paper I.

To get a crude theoretical estimate of $\epsilon(2p \rightarrow 1s^2 2s^2)$, we mixed in the 2P term of ($1s^2 2s 2p 3d$) configuration (double excitation). The $3d$ function is a single Slater orbital, ($r^2 e^{-\alpha r}$), with the radial part pulled into the region of the $2s$ and $2p$ orbitals. This gives an $\epsilon(2p \rightarrow 1s^2 2s^2)$ of -0.44 eV in B and -0.76 eV in Ne^{6+} already larger than previous estimates⁴ and we did not optimise the $3d$ orbital exponent nor scale the final wavefunction.¹⁰

b. $\epsilon(2p^2): 2p^2$ Correlation

Assuming $\epsilon(2p \rightarrow 1s^2 2s^2, A) = \epsilon(2p \rightarrow 1s^2 2s^2, A^+)$ for F, O, Ne, and neglecting some small effects which can be estimated from a full theoretical analysis (non-closed-shell many-electron theory; to be published) we get $\epsilon(2p^2) + \epsilon(2p \rightarrow 1s^2 2s^2) = -1.72$ eV (Fig. 1). $\epsilon(2p \rightarrow 1s^2 2s^2)$ lies between -0.4 eV and -0.8 eV. This -0.4 eV is Donath's¹¹ estimate and -0.8 eV is 50% of $\epsilon(2p \rightarrow 1s^2 2s^2)$ in Ne^{6+} . We take $\epsilon(2p \rightarrow 1s^2 2s^2, Ne) \approx \frac{1}{2} \epsilon(2p \rightarrow 2s^2 1s^2; Ne^{6+})$ because 50% of $\epsilon(2p \rightarrow 1s^2 2s^2, Ne^{6+})$ comes from $1s^2 2s-2p 3d(^2P)$ mixing and this configuration will not mix in $Ne(^1S)$. With these considerations we find that $\epsilon(2p^2)$ is about -1 ∓ 0.3 eV¹² less than the previous estimate⁴ of -1.72 eV.

CONCLUSIONS

The $1s^2 2s^2$ cores of B, C, and Ne are very different from the $1s^2 2s^2$ Be-like ion of these atoms (Fig. 1). $\epsilon(2s^2)$ in the Be-like ion is a nondynamical pair, and unlike the "dynamical" $1s^2$ pair (slowly convergent CI), is drastically reduced when we turn this core into say the $1s^2 2s^2$ core of the five-electron boron atom. The $\epsilon(2s^2)$ decreases from -1.13 eV in Be to -0.27 eV in Ne whereas the assumption of transferability of $1s^2 2s^2$ ion into the neutral atom would have led⁴ to the large value of $\epsilon(2s^2)$ in $Ne = -3.2$ eV. These pairs are nontransferable. The r_{12} calculations show that the dynamical part of $\epsilon(2s^2)$ remains negligible. Nonempirical calculation with e.g., αr_{12} , βr_{12}^2 , etc., are carried out easily one pair at a time. Putting r_{12} into the wavefunction avoids the slow convergence of CI and does

¹² Three-body effects may not be totally negligible in Ne itself and Kestner (private communication) estimates them to be 1 eV in Ne. We find them to be 0.07 eV in Ne^{6+} . Differences between these effects in Ne^{1+} and Ne will be much less and not important for our argument above.

not lead to difficult integrals even with the inclusion of all the orbital orthogonalizations.

$\epsilon(2p \rightarrow 1s^2 2s^2)$, the correlation of a $2p$ electron with the $1s^2 2s^2$ core, is large, ~ -1 eV. The nontheoretical comparison of the total $E_{\text{corr.}}$'s of the $1s^2 2s^2$ ions and the neutral atoms would have led, on the other hand,⁴ to the conclusion that $2s-2p$ correlations are negligible [$\epsilon(2p \rightarrow 1s^2 2s^2) = -0.25$ eV].⁴ The $\epsilon(2s^2)$ is not transferable from ions to neutral atoms and ions with more electrons. With the correct $\epsilon(2s^2)$, $\epsilon(2p^2)$ now comes out ~ -1 eV and not -1.72 eV.⁴

Since $\epsilon(2s^2)$ is so sensitive to the occupation of the $2p$ shell the $1s^2 2s^2$ core correlation will strongly depend on the state of the atom, e.g., 1S or 3P in carbon. The core energy will also depend on ionization and on molecule formation. Thus the usual assumption of the cancellation of inner shells is not valid except for $1s^2$. Correlation errors resulting from this assumption may be several electron volts. Such effects are being applied in this laboratory in connection with the prediction of excitation energies and molecular binding energies.

For heavier atoms, e.g., with $3s$, $3p$, $3d$ and higher d and f electrons we will find similar large exclusion effects making the inner ion cores of these atoms non-transferable. Again the usual assumption of the cancellation of inner cores will not hold. Also, as we found in the $2s-2p$ case above various "interorbital" correlations, e.g., between $3s$ and $3p$, $3p$ and $3d$, $3d$ and $4f$, etc., electrons of the larger atoms are expected to be appreciable. A rough idea about the importance of such correlations may be obtained from the magnitudes of the radial overlap integrals, e.g.,

$$\int R_{3d} R_{3p} r^2 dr,$$

etc., between the radial parts of the appropriate Hartree-Fock orbitals. Such correlations may need to be taken into account in the ligand-field theory of inorganic complexes.

$$\epsilon_{34}(2s^2) \leq \frac{2 \langle \mathcal{O}(2s(3)\alpha(3)2s(4)\beta(4)) \rangle, m_{34} \hat{u}_{34} \rangle + \langle \hat{u}_{34}, (e'_3 + e'_4 + m_{34} - \langle 2p_0(3)\alpha(3), g_{34} 2p_0(3)\alpha(3) \rangle P_{34} + \langle 2p_0(4)\beta(4), g_{34} 2p_0(4)\beta(4) \rangle P_{34}) \hat{u}_{34} \rangle}{1 + \langle \hat{u}_{34}, \hat{u}_{34} \rangle}. \quad (\text{A2})$$

P_{34} permutes Electrons 3 and 4. m_{34} contains the self-potentials but these cancel out in Eq. (A2). e'_3 is like e_3 , Eq. (10), but V_3 and ϵ_3 are from the traditional HF operators. The extra terms are differences in exchange potentials.

APPENDIX B. DETAILS OF r_{12} CALCULATIONS

The \hat{u}_{34} with the orbital orthogonalizations and r_{12} are easily handled. For example, with $2s_\alpha = 2s$, $2s_\beta = 2\bar{s}$,

$$u_{34}^0 = \mathcal{O}[2s(3)2\bar{s}(4)](\omega + \mu r_{34}), \quad (\text{B1})$$

$$\omega = -\mu \langle 2s(3)2s(3)2s(4)2s(4) r_{34} \rangle, \quad (\text{B2})$$

$g(3) = \langle 1s(4)2s(4) r_{34} \rangle_{x_4}$, $h(3) = \langle 2s(4)2s(4) r_{34} \rangle_{x_4}$, and

The exclusion effects on $2s^2$ correlation and the large $2s-2p$ correlation found in this paper should be significant also in π -electron theory. Because of these effects the σ core correlation in, say benzene, will change depending on which of the π orbitals are occupied in the particular electronic state. In addition the large $2s-2p$ correlations mean that now there should be appreciable $\sigma-\pi$ correlation¹⁸ interaction which will also depend on state.

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APPENDIX A. THEORY APPLIED TO SINGLE-DETERMINANT NONCLOSED SHELL STATES

For nonclosed shell single-determinant HF we cannot use Eq. (5) as it stands. The traditional HF potential, $V_i(\mathbf{x}_i)$, is not the same for every spin-orbital i . Roothaan's HF orbitals are identical with the traditional HF ones for the configurations dealt with in this paper. We used the operators of the traditional HF method but Roothaan's analytical representation⁷ of the orbitals. To see what happens to Eq. (5) for these single determinant nonclosed shell atoms we put, e.g., for boron $\chi = (2)^{-1} \mathcal{O}(1s\alpha 1s\beta \hat{u}_{34} 2p_0\alpha)$ and ϕ_0 into

$$E_{\text{corr.}} = E_{\text{exp.}} - E_{\text{HF}} \leq \frac{2 \langle \phi_0, (H - E_{\text{HF}})\chi \rangle + \langle \chi, (H - E_{\text{HF}})\chi \rangle}{1 + \langle \chi, \chi \rangle}. \quad (\text{A1})$$

We write out in detail the matrix elements of Eq. (A1). The final result after the appropriate cancellations looks very much like Eq. (5), though the variational pair energy expressions are not identical. For example, one has in boron

$$f(3) = \langle 2p_0(4)2s(4) r_{34} \rangle_{x_4}, \text{ we have}$$

$$\begin{aligned} \hat{u}_{34} = & u_{34}^0 - \mu \mathcal{O}[1s(3)2\bar{s}(4)g(4)] - \mu \mathcal{O}[2s(3)g(3)1\bar{s}(4)] \\ & - \mu \mathcal{O}[2s(3)2\bar{s}(4)h(4)] - \mu \mathcal{O}[2s(3)h(3)2s(4)] \\ & - 2\omega \mathcal{O}[2s(3)2\bar{s}(4)] - \mu \mathcal{O}[2p_0(3)2\bar{s}(4)f(4)] \\ & + \mu \mathcal{O}[1\bar{s}(4)1s(3)] \langle 1s(3)1s(4), 2s(3)2s(4) r_{34} \rangle \\ & + \mu \mathcal{O}[1s(3)2\bar{s}(4)] \langle 1s(3)2s(4), 2s(3)2s(4) r_{34} \rangle \\ & + \mu \mathcal{O}[2s(3)1\bar{s}(4)] \langle 2s(3)1s(4), 2s(3)2s(4) r_{34} \rangle. \end{aligned}$$

¹⁸ Sigma-pi correlation energies were discussed previously in terms of the core polarization theory (Ref. 6). They are also included in the many electron formulation of the Σ , Π separation and the π -electron problem (Papers I, II).

r_{34} occurs explicitly only in u_{34}^0 . The other terms are products of one electron functions, a convenient result.

All r_{12} integrals, except one, are reduced to a linear combination of integrals of the type¹⁴:

$$\int f(r_1) Y_l^m(\theta_1\phi_1) h(r_{12}) g(r_2) Y_{\lambda}^{\mu}(\theta_2\phi_2) dv_1 dv_2.$$

Rotating the co-ordinate system and integrating we obtain this integral in closed form. These expressions are then programmed.

¹⁴ J. L. Calais and P.-O. Löwdin, *J. Mol. Spectry*, **8**, 203 (1962).

The other integral contains three "inseparable" inter-electronic coordinates. We programmed the expressions derived by Öhrn and Nordling¹⁵ for the Yale IBM 709 computer. The general form of the integral is $\langle f_1(r_1) f_2(r_2) f_3(r_3) Y_k^m(1) Y_j^{\nu}(2) Y_l^{\mu}(3) r_{12}^{\lambda} r_{13}^{\mu} r_{23}^{\nu} \rangle$. This reduces to an infinite series. For spherically symmetrical integrands (Y_0^0) and $\lambda=1, \mu=-1, \nu=1$, the second term in the series is 3% of the first. For nonspherically symmetrical integrands (Y_1^0 and same λ, μ, ν) the second term is about 8% of the first.

¹⁵ Y. Öhrn and J. Nordling, *J. Chem. Phys.* **39**, 1864 (1963).

Scattering of High-Velocity Neutral Particles. XIII. Ar-CH₄; A Test of the Peripheral-Force Approximation*

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Collision cross sections have been measured for argon atoms with energies between 700 and 2100 eV, scattered in room-temperature methane. The results have been analyzed to obtain the average potential between an argon atom and a methane molecule,

$$\langle V(r) \rangle_{Av} = 936/r^{7.85} \text{ eV}, \quad 2.31 \text{ \AA} \leq r \leq 2.66 \text{ \AA}.$$

This result has been used as a test of combination-rule approximations by comparing it with the average potential calculated from previous measurements on He-CH₄, He-He, and Ar-Ar. The peripheral-force approximation gives consistent relations among the experimental results for these systems.

INTRODUCTION

THIS paper is concerned with the problem of obtaining information about the short-range forces between polyatomic molecules by the indirect procedure of scattering beams of fast neutral atoms from such molecules. Previous papers have reported the scattering of beams of He and Ar atoms by N₂ molecules,¹ and the scattering of beams of He atoms by CH₄ and CF₄ molecules.² These earlier studies indicated that it was a better approximation to assume that the force centers of the molecules were located on their peripheral atoms rather than to assume central forces for the molecules. The present measurements on Ar-CH₄ were made to check the consistency of these

conclusions through the agreement or disagreement with the results obtained with He-CH₄.

The ideal procedure would involve calculation of the average CH₄-CH₄ potential from scattering measurements on Ar-CH₄ and Ar-Ar, and comparison of the result with the average CH₄-CH₄ potential obtained from measurements obtained on He-CH₄ and He-He. This type of calculation, however, is extremely sensitive to the accuracy of the measured cross sections for Ar-CH₄ and Ar-Ar. For example, errors of the order of 5% in the Ar-CH₄ cross sections are magnified into errors of about tenfold in the derived CH₄-CH₄ potential. The effect results primarily from the extreme sensitivity of the index in the inverse power potential for CH₄-CH₄ to the corresponding indices in the experimental potentials for Ar-CH₄ and Ar-Ar. The present results were obtained some years ago and experimental difficulties limited the cross sections to those which could be obtained with a single (wide) detector. Their accuracy is therefore lower (of the order of 4% or 5%) than that obtainable from the

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¹ I. Amdur, E. A. Mason, and J. E. Jordan, *J. Chem. Phys.* **27**, 527 (1957).

² I. Amdur, M. S. Longmire, and E. A. Mason, *J. Chem. Phys.* **35**, 895 (1961).