TABLE VII. Molecular dimensions of stibine.

Isotopic species	Bond distance (Å)	Bond angle
Effective ground-state structure		
$^{121}SbH_3$, $^{123}SbH_3$	1.7102	91° 42′
$^{121}SbD_3$, $^{123}SbD_3$	1.7075	91° 42′
Substitution structure		
$^{121}SbD_3$: $^{123}SbD_3$, $^{121}SbH_3$	1.7039	91° 35′
$^{123}SbD_3$: $^{121}SbD_3$, $^{123}SbH_3$	1.7039	91° 35′
$^{121}SbH_3$: $^{123}SbH_3$, $^{121}SbD_3$	1.7032	91° 29′
$^{123}SbH_3$: $^{121}SbH_3$, $^{123}SbD_3$	1.7032	91° 29′

in accuracy by a factor of 10 over the previous values. Unfortunately, the new values cannot yet be used to advantage for giving more precise information about the molecular bonding or about the nuclear moment Q. The difficulty in interpretation comes mainly from the uncertainty in the atomic coupling per p electron in the group-V elements.[10] There is an additional complication because d-orbital hybridization, as well as s-orbital hybridization, occurs in the bonding orbitals of both As and Sb. As evidence for this, the nuclear quadrupole coupling, according to the best estimates of the eQq per p electron, indicates an s contribution of 12% to the bonding orbital of As in arsine and an s contribution of about 19% of Sb in stibine, whereas the nearly right-angle bonds in these molecules seem to indicate almost pure p bonding orbitals. Reconciliation of the bond angles and nuclear coupling can be achieved with spd-hybrid orbitals, but the required proportions are uncertain because of effects of ionic character, and because of approximations in the atomic coupling per p electron. A recent treatment of the molecular quadrupole coupling of group-V elements is given by Gordy and Cook.[8]

It is interesting to note from Tables III and VI that the nuclear quadrupole couplings of As and Sb are definitely larger in the deuterated species. This effect is not as easily understood as are the shorter bond lengths of the deuterated species, which can be ascribed to the smaller zero-point vibrations of the deuterium in a Morse-type potential field. The coupling differences reveal a definite alteration in the electronic structure of the molecule by the isotopic substitution.

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Symmetry-Adapted Pair Correlations in Ne, F^-, Ne^+, and F[†]

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The superposition-of-configurations method has been used to calculate, a single pair at a time, the pair correlation energies for Ne, Ne^+, F^-, and F. The approach is essentially a symmetry-adapted variation of Nesbet's formulation of the Bethe-Goldstone scheme for the atomic correlation problem, and the aim of this research was to test the usefulness of the method for predicting such physically observable quantities as ionization potentials and electron affinities. The calculations predict an ionization potential for neon of 21.52 eV, compared with a 21.56-eV experimental value, and a fluorine electron affinity of 3.47 eV, for which the experimental value is 3.45 eV.

INTRODUCTION

This paper reports the results of *ab initio* calculations of the correlation contributions to the binding energy of the final electron in the ground state of the 10-electron atoms Ne and F^-, i.e., the ionization potential of neon and the electron affinity of fluorine. The total correlation energies of both the $2s^22p^6$ (Ne, F^-) and $2s^22p^5$ (Ne^+, F) systems were estimated from "pair-at-a-time" calculations of the correlation using the superposition-of-configuration (SOC) method. The binding energies were obtained by simply differencing the resulting estimates of the "exact" total energies.

These calculations are based on several physical assumptions. First, it is assumed that the total energy can be well approximated by

$$E = E_0 + \sum_n \epsilon_n + \sum_{mn} \epsilon_{mn} \ , \qquad (1)$$

where E_0 is the Hartree-Fock (HF) total energy and ϵ_{mn} is the correlation energy of the mn pair. The ϵ_n terms represent single-particle correlations which may, or may not, be important, depending on the shell structure of the atom and the detailed formulation of the correlation problem. The second and probably most important assumption supposes that these ϵ's can be calculated independently by a set of separate SOC calculations; i.e., one computes, using the full Hamiltonian, a set of variational wave functions of the form

$$\psi_{mn} = \Phi_0 + \sum_{ij} a_{mn}^{ij} \Phi_{mn}^{ij} \qquad (2)$$

and identifies the lowering of the total energy in each case with the corresponding correlation energy increment ϵ of Eq. (1). In (2), Φ_0 is the N-electron HF wave function, and the notation such as Φ_{mn}^{ij} refers to configurations where one has substituted for the mn pair in Φ_0 a set of virtual orbitals adequate to converge on the energy to the desired accuracy. Furthermore, in the present calculations the substitutions refer to symmetry-adapted pairs, i.e., a pair of space orbitals of a given angular-momentum coupling are substituted by a set of virtual orbitals and with the angular momenta recoupled to give the appropriate over-all LS symmetry. For example, to calculate the $2p^2\ {}^3P$ correlation energy in neon, one adds to the $2p^6$ HF term configurations of the type $(2p^4\ {}^3P)\ (nl^2\ {}^3P)\ {}^1S$.

Precisely to what extend one can rigorously formulate a theoretical basis for this procedure is somewhat problematical, and ultimately the justification may simply be the pragmatic one of how well it works in practice. There is no paucity of theories in the literature which can be invoked to support this kind of calculation. Sinanoğlu has discussed extensively the correlation problem in his many-electron theory (MET) of atoms and molecules.[1] By making suitable approximations he is able to decouple the pair equations leading to an algorithm which, for a SOC expansion, is practically the same as that described here, and the present calculations therefore are at least in the spirit of MET. Sinanoğlu and his co-workers have also made extensive semiempirical calculations of correlation energies.[2] Another variational pair theory has been proposed by Szász[3] which, however, is less compromising in its constraints and approximations and thus leads to a quite complicated set of equations. Kelly has also made extensive calculations of correlation energies by adapting many-body perturbation theory to the atomic problem.[4] Finally, mention should be made of the interesting and very recent work by Boys and Handy[5] on the transcorrelation method, which is quite different from any of the approaches just described in that it attempts to obtain directly an approximate solution of the wave equation. This method appears to hold considerable promise for just such problems as are treated here.

However, the formulation most closely akin to the present study is probably Nesbet's adaptation of the Bethe-Goldstone procedure.[6] Nesbet has described such pair-at-a-time calculations as a variational approach to solving the Bethe-Goldstone equations, and he has had remarkable success in the completely *ab initio* calculation of ground-state atomic correlation energies.[7] His algorithm is essentially the same as the one used here, with the one technical difference that his pair correlations refer to excitation of explicit spin orbitals from the HF determinant. His pair calculations thus do not yield pure LS states, although it is implicit in the basic theory that the final result will end up as an eigenfunction of L^2 and S^2.

Since the elemental pairs are defined somewhat differently, it is to be expected that in the incremental summation there will be some differences between Nesbet's results and those reported here. It was partly to investigate the difference in using spin-orbital and symmetry-adapted pairs that these calculations were undertaken. A similar calculation on neon using symmetry-adapted pairs has recently been done by Viers, Harris, and Schaefer (VHS),[8] who find fairly substantial differences with Nesbet's Bethe-Goldstone results. The VHS calculation differs from the present one in that they calculated all their symmetry-adapted pairs for a given orbital pair in one diagonalization; e.g., the $2s2p\ {}^1P$ and $2s2p\ {}^3P$ pairs are calculated together as one intershell pair, whereas here they are done separately.

The more important reason for doing these calculations, however, concerns the question of how well one can do in predicting physically observable quantities. Since such single-pair calculations seem to be proving so successful at predicting total correlation energies, the obvious observable for which there is the most hope is simply the energy difference of the atom and ion, i.e., the ionization potential or electron affinity. Atomic (or molecular) electron affinities represent one area where this approach may well have real predictive value, particularly for complex atoms where there is little

TABLE I. Calculated correlation energy increments (in a.u.) for Ne and F^-.

Electron pair	ΔE(Ne) This work	Nesbet (Ref. 7)	VHS (Ref. 8)	$\Delta E(F^-)$ This work
$2p^2\,{}^3P$	0.0900			0.0961
$2p^2\,{}^1D$	0.0825			0.0904
$2p^2\,{}^1S$	0.0436			0.0450
$2p$-$2p$ correlation	0.2161	0.2248	0.1856	0.2315
$2s2p\,{}^1P$	0.0490			0.0526
$2s2p\,{}^3P$	0.0231			0.0268
$2s$-$2p$ correlation	0.0721	0.0816	0.0756	0.0793
$2s^2\,{}^1S$	0.0105	0.0108	0.0113	0.0110
$1s^2\,{}^1S$	0.0394	0.0399	0.0390	0.0397
$1s2p$ correlation	0.0183	0.0199	0.0190	0.0154
$1s2s$ correlation	0.0048	0.0051	0.0050	0.0047
Total correlation energy	0.3612	0.3821	0.3356	0.3817
HF total energy	−128.5471			−99.4594
"Exact" total energy	−128.9083	−128.9292	−128.8827	−99.8411

data, such as Ti^-, V^-, Cr^-, etc.[9] Calculations of affinities along these lines have been attempted by Sinanoğlu and co-workers with moderate success.[1] However, this may well be due to the semiempirical nature of the correlation estimates leading to accumulation of the concomitant small errors.

This paper, therefore, reports symmetry-adapted pair-at-a-time calculations of the correlation energies of Ne, Ne^+, and F, F^-. The calculations are all *ab initio* calculations done in the same way on all systems and at the same level of numerical approximation throughout. The point, of course, is to test out the pair-correlation approach for systems for which there is reliable experimental data.

RESULTS AND DISCUSSION

The calculations are based on expansion method HF wave functions which have been adequately described elsewhere.[10,11] The basis set for the HF orbitals consists of five s- and four p-type Slater orbitals (STO). For the SOC calculations, this set was enlarged both by the addition of higher symmetries (d and f functions) and by augmenting the s and p basis. In every case, the exponents of the added functions were optimized. For the L-shell correlation, the orbital parameter optimization was done on the $2s2p\,{}^1P$ pair; pseudonatural orbitals were generated for this pair and subsequently used for all other L-shell pairs.[12,13] For the K-shell and K-L intershell correlation, the HF basis was augmented with basis functions whose exponents were appropriate to spatially span these regions of the atom. In fact, for the K shell the basis set was augmented by the same functions as Nesbet used in his neon and fluorine calculations, although the set was somewhat more truncated, since these calculations started from a larger HF basis.

In the case of fluorine and the neon positive ion, where the ground-state configuration is $2s^22p^5$, there are some single space-orbital substitutions which make important contributions, e.g., $(2s3d\,{}^3D)2p^5$. In a symmetry-adapted formulation it is not possible to assign these terms unambiguously to any particular electron pair, and their effect has been calculated here as a separate single-particle type of correlation contribution. These kinds of terms correspond to the most important of the "semi-internal" correlations in Sinanoğlu's formulation of the problem.[1]

The result of the pair calculations of Ne and F^- are given in Table I and compared with Nesbet and VHS, which are the only other comparable *ab initio* calculations.[14] It is clear that the present symmetry-adapted calculation underestimates the correlation relative to the Bethe-Goldstone spin-orbital pair calculation. On the other hand, the symmetry-adapted calculation of VHS underestimates the correlation relative to the present one, although the differences are not terribly large. In part, these differences are no doubt due to differences in basis sets and the SOC expansion lengths. Part of the difference with VHS is also probably due to the fact that they have grouped different symmetry-adapted pairs for the same space-orbital pair in one diagonalization and thus have done fewer independent pair calculations. Precisely how much of the correlation energy has been recovered depends on one's empirical estimate of the correlation energy, and it appears that the present calculations are getting about 95% of the correlation en-

TABLE II. Calculated correlation energy increments (in a.u.) for Ne^+ and F.

Electron pair	$\sum \Delta E(Ne^+)$ This work	$\sum \Delta E$(F) This work	Nesbet (Ref. 7)
$2p^2$	0.1420	0.1465	0.1510
$2s2p$	0.0546	0.0590	0.0884
$2s^2$	0.0106	0.0106	0.0119
$1s^2$	0.0390	0.0394	0.0398
$1s2p$	0.0178	0.0152	0.0164
$1s2s$	0.0050	0.0049	0.0055
"Semi-internal"	0.0297	0.0280	0.0021
Total correlation energy	0.2987	0.3037	0.3151
HF total energy	−127.8178	−99.4093	···
"Exact" total energy	−128.1165	−99.7131	−99.7244

TABLE III. Computed and experimental values of the neon ionization potential and fluorine electron affinity.

					ΔE (eV)	
		ΔE(a.u.)	This work [a]	Transcorrel[a,b]	MET [c]	Expt
Ne	HF	0.7293	19.81	···	···	···
	Correlated	0.7918	21.52	21.55	···	21.56 [d]
F^-	HF	0.0501	1.34	···	···	···
	Correlated	0.1280	3.47	···	3.23	3.448

[a] These values have been adjusted for the observed doublet splitting of $2s^2 2p^5$. See text.
[b] Reference 5.
[c] Reference 17.
[d] Reference 15.
Reference 16.

ergy for neon.

The analogous calculations for Ne^+ and F are shown in Table II. Since for these open-shell systems there are so many independent pairs, even in the symmetry-adapted calculation, and the detailed breakdown of the correlation does not appear to be important, only the totals for the different space-orbital pairs are given. It should be noted that these totals represent the summations of independently calculated correlation energies. For neutral fluorine the results are again compared with Nesbet, and again the correlation energy is somewhat underestimated relative to the Bethe-Goldstone calculations.

Table III now gives the results of combining the above two sets of calculations to give predicted values for the neon ionization potential and fluorine electron affinity. It should be noted that in the column where the results are given in eV the theoretical results have been shifted by the experimental value of the center of gravity of the doublet splitting of $2s^2 2p^5$. This has been done to give a direct comparison to the experimental values, whicl are measured relative to the $\frac{3}{2}$ component of the ^2P state. Table III also includes comparisons with experimental data[15,16] as well as other comparable calculations.[17] It is clear that the results appear to be quite good, and unless this happens to be fortuitous they strongly suggest the great utility of such individual pair calculations for a large number of interesting problems. One has here calculated, to rather high precision, the binding energy of the last electron as the difference of the two large total energies. It should be commented at this point that had the K-shell and K-L intershell correlation energies been omitted the results would not have been substantially different (21.50 and 3.46 eV for Ne and F^-, respectively). The calculations also indicate, incidentally, that, contrary to some recent observations, there appears to be no need whatsoever for considering three and more body effects.[18]

While it will always be necessary to do a reasonably thorough job on each of the pairs, it appears that as long as one calculates to about the same level of accuracy it should be possible to reap considerable benefits from such individual pair-correlation calculations. Molecular binding energies, complex atom electron affinities, as well as molecular electron affinities are a few problems which are likely to be amenable to such an approach. At least the present results indicate the desirability of further investigations into the question.

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