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Self-Consistent-Field Wave Functions for Hole States of Some Ne-Like and Ar-Like Ions*†‡

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Analytic self-consistent-field (SCF) wave functions were computed for the ground states of the closed-shell atomic systems F^-, Ne, and Na^+, and Cl^-, Ar, and K^+; and for those ground and excited states of the open-shell systems which are obtained by removing a single electron from any one of the occupied shells of these closed-shell systems. Details of the calculation of the functions are presented, with emphasis on a justification of the procedures used for the calculations for excited states. A high accuracy is obtained; the calculations for the closed-shell systems give the most accurate analytic SCF wave functions which have yet been reported. Ionization potentials are calculated and compared with experimental values. Computed ionization potentials for the removal of a $2s$ electron from Cl^-, Ar, and K^+, for which no direct experimental data are available, are estimated to be accurate to 1%. It is found that the removal of an electron from the outermost s shell increases the correlation energy, in contradiction to the predictions of a recently proposed semiempirical scheme for estimating the correlation energy. For example, the magnitude of the correlation energy of the lowest ${}^2S$ state of Ar^+ is ~4 eV greater than the magnitude of the correlation energy of neutral Ar. The effect of the nonzero off-diagonal Lagrangian multipliers is considered and found to be important for the inner shell hole states.

I. INTRODUCTION

ANALYTIC self-consistent-field (SCF) functions are presented for the ground states of the closed-shell atomic systems F^-, Ne, Na^+, Cl^-, Ar, and K^+, for the $1s^22s^22p^5$, $1s^22s2p^6$, and $1s2s^22p^6$ configurations of F, Ne^+, and Na^{++} (which, for convenience, we refer to as the $2p$-hole, $2s$-hole, and $1s$-hole states, respectively) and for the $1s^22s^22p^63s^23p^5$, $1s^22s^22p^63s3p^6$, $1s^22s^22p^53s^23p^6$, $1s^22s2p^63s^23p^6$, and $1s2s^22p^63s^23p^6$ configurations of Cl, Ar^+, and K^{++} (which we refer to as the $3p$-hole state, $3s$-hole state, etc.). These states are of interest for x-ray emission and absorption phenomena and also, for example, for calculating the effect of the electronic charge distribution on electron capture by the nucleus.[1] Ionization potentials, expectation values of r and r^2 for the SCF orbitals and overlap integrals between *total* wave functions not orthogonal by symmetry are given. In a later paper, transition probabilities for photon emission computed using the SCF wave functions listed above will be given.

The SCF wave functions were calculated using the Roothaan analytic expansion method. This method was developed first for closed-shell systems and then extended to a large class of open-shell systems.[2,3] In its present form the method will treat a system with any number of open shells provided that there is at most one open shell for each one-electron symmetry species.[3] Reliable and accurate numerical techniques have been developed and incorporated into computer programs for calculating atomic SCF wave functions by this method.[3]

In the Roothaan expansion method, the SCF orbitals φ_{nlm} are given in terms of *basis functions* $\chi_{p,lm}$ by

$$\varphi_{nlm}=\sum_p \chi_{p,lm}C_{nl,p}\,, \qquad (1)$$

where *nlm* are the usual one-electron quantum numbers for atoms. The basis functions are given by

$$\chi_{p,lm}(r,\theta,\phi)=R_{lp}(r)Y_{lm}(\theta,\phi)\,; \qquad (2)$$

where the $Y_{lm}(\theta,\varphi)$ are normalized spherical harmonics, and the radial functions $R_{lp}(r)$ are normalized, nodeless Slater-type orbitals (STO's),

$$R_{lp}(r;n_{lp}\zeta_{lp})=[(2n_{lp})!]^{-1/2}(2\zeta_{lp})^{n_{lp}+\frac{1}{2}}r^{n_{lp}-1}e^{-\zeta_{lp}r}\,. \qquad (3)$$

The integer n_{lp} is called the principal quantum number of the basis function and ζ_{lp} the orbital exponent. [Care should be taken not to confuse the two different uses of "principal quantum number." The principal quantum number of an orbital is the label which distinguishes that orbital from other orbitals of the same symmetry species (l) and subspecies (m). The principal quantum number of an STO is merely a flexible parameter of a basis function.]

Many accurate SCF calculations for ground and low-lying excited states of atoms have been performed using

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[1] See, for example, J. N. Bahcall, Phys. Rev. **129**, 2683 (1963); **131**, 1756 (1963).

[2] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951); **32**, 179 (1960).

[3] C. C. J. Roothaan and P. S. Bagus, *Methods in Computational Physics* (Academic Press Inc., New York, 1963), Vol. II.

the Roothaan analysis.[4–8] The functions presented herein are the first analytic SCF calculations for x-ray excited states of atoms. To our knowledge, of the very few numerical calculations performed, the only numerical Hartree-Fock (HF) calculations for such states that correctly take exchange into account are those of Sureau and Berthier on Al.[9]

II. THE SCF PROCEDURE FOR EXCITED STATES

An SCF solution for a ground state or an excited state which is the lowest state of a symmetry species has an unambiguous interpretation. The SCF total energy is an upper bound to the true energy and would be equal to it if and only if the SCF wave function were an exact solution of the Schrödinger equation. The SCF total energy is also the lowest total energy which can be obtained with the restricted form of the trial wave function used. An SCF wave function for an excited state which is not the lowest state of a symmetry species would have a corresponding interpretation if it were constrained to be orthogonal to the exact wave functions for all the states of lower energy. This constraint cannot be imposed in practice. One procedure would be to approximate this constraint by requiring orthogonality to the SCF wave functions for the lower states. This, however, is not done; no explicit requirement of orthogonality to lower SCF states is made at all.[7,10] Instead, we rely on the physical model for the form of the SCF excited-state wave function to guarantee near-orthogonality to the SCF wave functions for lower states. This physical model is, of course, the orbital or shell structure of the atom.

The only constraint which is imposed to obtain an excited-state wave function is the specification of the electronic configuration. For a 1*s*-hole state, for example, the HF operators are constructed on the assumption that the 1*s* orbital is occupied by only one electron. Eigenvectors of the HF operators are obtained and iterations are performed in the usual way until the condition of self-consistency is met, but the assumption that the 1*s* orbital is singly occupied is maintained throughout the process. The singly occupied 1*s* orbital, chosen at each iteration, is the eigenvector (of the appropriate HF operator) with the lowest orbital energy. This orbital is chosen because it is the orbital which is most similar to a hydrogenic 1*s* orbital. The choices of the 2*s* and 3*s* orbitals are made for similar reasons. (The practical basis for the choices made at each iteration in the process of the computation is that the eigenvectors chosen are the ones which most closely resemble the vectors used to construct the HF operators.)

TABLE I. Overlap integrals between total SCF wave functions of the *nl*-hole states.

		F^-	Ne	Na^+
^2S States	$\langle\Psi(2s\text{ hole})\|\Psi(1s\text{ hole})\rangle$	0.003984	0.003380	0.002876
		Cl^-	Ar	K^+
^2P States	$\langle\Psi(3p\text{ hole})\|\Psi(2p\text{ hole})\rangle$	0.009428	0.008299	0.007285
^2S States	$\langle\Psi(3s\text{ hole})\|\Psi(2s\text{ hole})\rangle$	0.006062	0.005469	0.004906
	$\langle\Psi(3s\text{ hole})\|\Psi(1s\text{ hole})\rangle$	0.000514	0.000486	0.000457
	$\langle\Psi(2s\text{ hole})\|\Psi(1s\text{ hole})\rangle$	0.001264	0.001131	0.001018

We may justify this procedure by noting that the electron density of a complex atom does not change drastically in going from ground to excited states so that the corresponding HF operators are not sufficiently different and the SCF wave functions for excited states are very nearly orthogonal to SCF wave functions for lower states. The 3*s*-hole state of Ar is the lowest ^2S state of Ar^+; the 1*s*-hole state, a very highly excited ^2S state, is 3200 eV above the 3*s*-hole state. Even for this extreme case, the overlap integral between the many-electron SCF wave functions, $\langle\Psi_{SCF}(1s\text{ hole})|\Psi_{SCF}(3s\text{ hole})\rangle$, is 5×10^{-4}. The requirement that the 1*s*-hole SCF wave function be orthogonal to the 3*s*-hole SCF wave function would produce only a very small change in the 1*s*-hole wave function. Further, since the 3*s*-hole SCF wave function is only an approximate eigenfunction, we do not know whether the constraint of orthogonality would improve or worsen the 1*s*-hole wave function. Overlap integrals between the many-electron SCF wave functions which are not orthogonal by symmetry are given in Table I.[11]

For a certain class of the states formed by exciting a *single* electron, it is possible to state easily tested conditions to determine whether the SCF total energy is an upper bound to the true energy.[12] Unfortunately, the inner shell hole states are not in this class; in Sec. IVB, however, we show by comparing experimental and computed ionization potentials that the SCF energies for these states are, in fact, greater than the true energies. The justification of the procedure of optimizing the exponents of the basis set by minimizing the total energy will be discussed in Sec. IVB. This problem occurs only for expansion SCF calculations and is not encountered when the HF equations are solved numerically.

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[4] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960).

[5] L. M. Sachs, Phys. Rev. **124**, 1283 (1961).

[6] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962).

[7] C. C. J. Roothaan and P. S. Kelly, Phys. Rev. **131**, 1177 (1963).

[8] P. S. Bagus, T. L. Gilbert, C. C. J. Roothaan, and H. D. Cohen (to be published).

[9] A. Sureau and G. Berthier, J. Phys. Radium **24**, 672 (1963).

[10] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

[11] M. Cohen and A. Dalgarno, Rev. Mod. Phys. **35**, 506 (1963) and D. Layzer, Phys. Rev. **132**, 735 (1963) have investigated the overlap of SCF excited states of the same symmetry using expansions of SCF wave functions in powers of $1/Z$ and find that the overlap is zero to order $(1/Z)^2$.

[12] P. S. Bagus (to be published).

III. DETAILS OF THE CALCULATION OF THE SCF WAVE FUNCTIONS

In order to obtain analytic SCF orbitals which are good approximations to the exact HF[13] orbitals, it is necessary to use a basis set which very nearly spans the true HF manifold. The advantage of the expansion method is greatest when a relatively small basis set can be used to do this. In order to use small basis sets without sacrifice of accuracy, care must be taken to obtain an optimum set of exponents which give the lowest possible SCF total energy.

Our method for varying the exponents in order to find optimum values is to perform a number of complete SCF calculations for different values of the exponents and to interpolate between them to find the values which minimize the SCF total energy. This optimization procedure is performed automatically by the SCF computer program.[3] While we do not explicitly solve variational equations for the exponents with this method, we do obtain a stationary value of the expectation value of the energy with respect to the exponents being varied. The particular stationary value which we obtain is a minimum. Explicit variational equations for the exponents have been given by Dehn.[14] The equations for the exponents appear to be difficult to solve, and our *brute-force* variation of the exponents has proved to be a quite satisfactory procedure.

While the exponents, being continuous parameters, were optimized by continuous variation, the principal quantum numbers of the basis functions, being integers, need to be chosen more or less arbitrarily. Our preference was to choose principal quantum numbers for the STO's which are to represent the nth loop of a series of orbitals so that the STO's would have the same power of r as hydrogenic functions representing that loop have. Thus for the states of F, Ne, and Na we used $2p$ STO's to represent the $2p$ orbital; and for the states of Cl, Ar, and K we used $3s$ STO's to represent the outer loop of the $3s$ orbital. This was by no means a hard and fast rule and we often deviated from it. The deviations were based on limited experimentation with other values and were usually made in order to obtain relatively small improvements in the energy or to avoid near redundancy in the basis set during the exponent variation.

It is important when working with basis sets of limited size to build up the basis set systematically to the final accurate set. The initial calculation for a state should be made with a rather small basis set. This set cannot give an accurate representation of the exact HF wave function, but for a small set it is quite easy to find the optimum values of the exponents. Additional exponents are then introduced, usually one at a time, and the exponents reoptimized. It is not sufficient to optimize only the exponents of the new basis functions; the exponents of old functions must also be adjusted when a new function is added. This build-up procedure provides an indication of the accuracy of the SCF solution (from the successive energy increments obtained with each addition) and also provides information for making an educated guess about the need for additional basis functions. The intermediate basis sets are often useful in themselves.

Because of the many SCF calculations involved in the optimization of the basis set, it is essential to apply the experience gained in the calculation of one state to the calculation of similar states of the same or neighboring atoms. The calculation of the functions of a series of states should be done systematically. The function for each state should not be computed as a separate problem. Linear extrapolations or interpolations of the exponents for states already computed provide an extremely good starting point for the exponent variations which determine the optimized exponents for a nearby state. In fact, if an extrapolation or interpolation to a neighboring state fails to work well, one has excellent reason to suspect an error in one of the previously computed states. Although the calculation of the SCF wave function for a single state is laborious and time consuming, the calculation of wave functions for a series of states is fairly economical.

The minimization of the total energy was the fundamental criterion used to choose the basis sets for the SCF functions. The analytic SCF orbitals determined by using this criterion are not uniformly good approximations to the exact HF orbitals. The orbitals of the electrons which contribute most to the total energy, the core or inner shell electrons, are determined most accurately. The orbitals of the electrons which contribute least to the total energy, the valence or outer shell electrons, are determined least accurately.

Because it is more difficult to obtain accurate orbitals for the $3s$ and $3p$ shells than for the inner shells, we paid close attention to small changes in the SCF total energy when choosing the basis functions used to represent the outer loops of the $3s$ and $3p$ orbitals of the states of the Cl, Ar, and K ions. Small improvements in the total energy obtained in fitting these loops are at least as important for the general quality of the wave function as larger improvements obtained when fitting the inner shell orbitals. It was also necessary to look for small energy improvements when the most accurate functions were computed in order to fit the tails of the orbitals properly. The tails of the orbitals make the smallest contribution to the total energy. Small expansion sets fit the orbitals in the regions where they are large at the expense of the behavior of their tails, and larger basis sets must be chosen carefully so that the tails will be represented properly.

The techniques outlined above make it possible to efficiently compute accurate expansion SCF wave functions with the computer program described in Ref. 3.

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[13] The notations SCF and HF will be used almost interchangeably. When we wish to distinguish between analytic expansion orbitals as opposed to exact solutions of the HF equations, we will use the notation SCF orbitals as opposed to HF orbitals.

[14] J. T. Dehn, J. Chem. Phys. 37, 2549 (1962).

Table II. SCF orbitals and energies for F$^-$, Ne, and Na$^+$, and *nl*-hole states of F$^-$, Na, and Na$^+$, accurate basis sets.

	F$^-$(^1S)	F(^2P) 2p hole	F(^2S) 2s hole	F(^2S) [a] 1s hole	Ne(^1S)	Ne$^+$(^2P) 2p hole	Ne$^+$(^2S) 2s hole	Ne$^+$(^2S) [a] 1s hole	Na$^+$(^1S)	Na^{++}(^2P) 2p hole	Na^{++}(^2S) 2s hole	Na^{++}(^2S) [a] 1s hole
E	−99.45944	−99.40933	−98.53123	−74.52412	−128.5471	−127.8178	−126.7348	−96.62571	−161.6770	−159.9974	−158.7088	−121.7424
V/T	−1.999998	−1.999996	−1.999999	−2.000000	−1.999998	−2.000003	−2.000003	−1.999997	−2.000001	−2.000003	−2.000003	−2.000002
$\zeta_1(1s)$	13.958	14.201	13.901	15.308	15.439	15.409	15.231	16.768	15.949	15.329	15.530	18.164
$\zeta_2(1s)$	7.936	7.938	7.893	8.371	8.806	8.811	8.771	9.179	9.439	9.597	9.289	9.982
$\zeta_3(3s)$	9.873	9.962	9.901	10.713	10.995	10.967	10.951	11.732	11.624	11.374	11.355	12.750
$\zeta_4(2s)$	3.426	3.332	3.288	3.522	3.764	3.824	3.758	4.070	4.384	4.462	4.372	4.566
$\zeta_5(2s)$	2.183	2.057	2.078	2.175	2.301	2.526	2.537	2.670	2.811	3.047	3.058	3.153
$\zeta_6(2s)$	1.500	...	...	...	...	...	...	...	...	...	...	...
$\zeta_1(2p)$	9.788	9.435	8.793	6.809	10.542	12.548	12.000	10.835	12.048	13.437	12.730	10.580
$\zeta_2(2p)$	4.446	4.249	4.181	4.058	4.956	5.759	5.718	5.567	5.703	6.030	5.939	5.829
$\zeta_3(2p)$	2.595	2.356	2.324	2.285	2.793	3.476	3.436	3.279	3.336	3.649	3.503	3.300
$\zeta_4(2p)$	1.511	1.434	1.404	1.487	1.623	2.086	2.047	2.142	2.146	2.522	2.433	2.409
$\zeta_5(2p)$	0.869	...	...	...	...	...	...	...	...	...	...	...
ϵ_{1s}	−25.82961	−26.38265	−26.42060	−29.53630	−32.77233	−33.61235	−33.61629	−37.16999	−40.75972	−41.86280	−41.83081	−45.82043
Cusp	−9.02404	−9.02760	−9.02411	−9.01167	−10.02496	−10.02477	−10.02401	−10.01652	−11.01520	−11.00906	−11.01874	−11.02114
$C_{1s,1}$	0.08975	0.08419	0.09403	0.04171	0.09218	0.09256	0.09927	0.05077	0.13371	0.14458	0.15929	0.05967
$C_{1s,2}$	0.94747	0.95503	0.94586	0.99591	0.94891	0.94804	0.94216	0.99596	0.91835	0.89061	0.89684	0.99466
$C_{1s,3}$	−0.04015	−0.04226	−0.04308	−0.05444	−0.04499	−0.04442	−0.04548	−0.06476	−0.05827	−0.03891	−0.06368	−0.07315
$C_{1s,4}$	0.00377	0.00301	0.00374	0.01684	0.00308	0.00299	0.00377	0.01303	0.00156	0.00420	0.00238	0.01003
$C_{1s,5}$	−0.00083	−0.00013	0.00014	0.01247	−0.00003	−0.00018	0.00004	0.01332	0.00060	−0.00067	0.00061	0.01359
$C_{1s,6}$	0.00050	...	...	...	...	...	...	...	...	...	...	...
ϵ_{2s}	−1.07458	−1.57245	−1.70583	−1.74534	−1.93031	−2.61917	−2.75317	−2.85349	−3.07368	−3.93054	−4.06585	−4.22305
Cusp	−9.06777	−9.06608	−9.07213	−9.04294	−10.05351	−10.05387	−10.06436	−10.04150	−11.03456	−11.02316	−11.02905	−11.02846
$C_{2s,1}$	0.00560	0.00519	0.00439	0.01255	0.00645	0.00718	0.00611	0.01275	0.00581	0.01251	0.00333	0.01304
$C_{2s,2}$	−0.27435	−0.28031	−0.28538	−0.31567	−0.28821	−0.29829	−0.30146	−0.33112	−0.30875	−0.32313	−0.32328	−0.34522
$C_{2s,3}$	−0.02865	−0.02805	−0.02678	−0.03023	−0.02632	−0.02831	−0.02674	−0.02983	−0.02404	−0.03062	−0.02199	−0.02807
$C_{2s,4}$	0.49528	0.56794	0.59904	0.57594	0.56972	0.52685	0.56055	0.51259	0.49163	0.44384	0.47343	0.47638
$C_{2s,5}$	0.47665	0.52863	0.49531	0.52319	0.53066	0.56743	0.53148	0.58614	0.61232	0.65800	0.62678	0.62255
$C_{2s,6}$	0.13770	...	...	...	...	...	...	...	...	...	...	...
ϵ_{2p}	−0.18098	−0.72994	−0.70271	−0.87141	−0.85034	−1.60663	−1.55267	−1.81602	−1.79719	−2.74429	−2.66306	−3.01964
Cusp	−4.53215	−4.51761	−4.46597	−4.40926	−5.00030	−5.06068	−5.03668	−5.00617	−5.52223	−5.58134	−5.55100	−5.49840
$C_{2p,1}$	0.00800	0.01055	0.01380	0.04764	0.00930	0.00408	0.00473	0.00566	0.00784	0.00509	0.00619	0.01168
$C_{2p,2}$	0.20342	0.26789	0.27605	0.35674	0.24154	0.13743	0.14248	0.23853	0.23017	0.19601	0.21089	0.30104
$C_{2p,3}$	0.39809	0.49083	0.48600	0.47736	0.48233	0.42831	0.43100	0.45718	0.45558	0.42481	0.46037	0.57139
$C_{2p,4}$	0.36280	0.32561	0.32218	0.21207	0.36532	0.50305	0.49736	0.37235	0.38418	0.43417	0.38511	0.17715
$C_{2p,5}$	0.17010	...	...	...	...	...	...	...	...	...	...	...

[a] States which are not the lowest of a symmetry species.

TABLE III. SCF orbitals and energies for Cl$^-$ and *nl*-hole states of Cl$^-$, accurate basis sets.

	Cl$^-$(^1S)	Cl(^2P) $3p$ hole	Cl(^2S) $3s$ hole	Cl(^2P) [a] $2p$ hole	Cl(^2S) [a] $2s$ hole	Cl(^2S) [a] $1s$ hole
E	−459.5768	−459.4820	−458.9167	−452.3349	−449.7655	−356.2822
V/T	−1.999999	−2.000000	−2.000001	−2.000001	−2.000001	−2.000004
$\zeta_1(1s)$	19.955	19.840	19.830	19.955	19.955	20.000
$\zeta_2(2s)$	14.545	14.650	14.670	14.530	14.505	16.500
$\zeta_3(3s)$	16.000	16.000	16.000	16.000	16.000	18.000
$\zeta_4(3s)$	9.951	9.940	9.932	9.684	9.954	10.166
$\zeta_5(2s)$	5.748	5.745	5.743	5.867	6.010	6.062
$\zeta_6(3s)$	2.823	2.904	2.878	3.140	3.030	3.167
$\zeta_7(3s)$	1.651	1.826	1.842	1.970	1.923	1.982
$\zeta_1(2p)$	15.380	15.440	15.525	16.345	16.600	16.900
$\zeta_2(2p)$	7.535	7.550	7.555	7.790	7.845	8.310
$\zeta_3(2p)$	4.385	4.415	4.405	4.600	4.615	4.980
$\zeta_4(4p)$	7.200	7.200	7.200	7.700	7.700	8.000
$\zeta_5(3p)$	2.612	2.663	2.653	2.852	2.861	2.926
$\zeta_6(4p)$	1.826	1.976	1.932	2.091	2.100	2.136
$\zeta_7(3p)$	0.920	1.236	1.191	1.307	1.310	1.311
ϵ_{1s}	−104.50546	−104.88431	−104.95559	−106.27042	−106.04136	−112.50264
Cusp	−17.00483	−17.00224	−17.00306	−17.00187	−17.00641	−17.00392
$C_{1s,1}$	0.76554	0.77219	0.77275	0.76588	0.76542	0.77416
$C_{1s,2}$	0.43218	0.40836	0.40543	0.43389	0.43475	0.32382
$C_{1s,3}$	−0.16990	−0.15323	−0.15094	−0.17190	−0.17195	−0.07287
$C_{1s,4}$	0.00060	0.00227	0.00272	−0.00055	−0.00072	0.00487
$C_{1s,5}$	0.00005	−0.00060	−0.00082	0.00041	0.00107	0.01344
$C_{1s,6}$	0.00003	0.00013	0.00015	−0.00006	−0.00006	−0.00217
$C_{1s,7}$	−0.00004	−0.00009	−0.00011	−0.00001	0.00000	−0.00191
ϵ_{2s}	−10.22916	−10.60741	−10.66547	−11.32032	−11.47391	−11.83135
Cusp	−16.99333	−16.99389	−16.99236	−16.98104	−17.02706	−16.94919
$C_{2s,1}$	−0.21448	−0.21639	−0.21622	−0.21855	−0.21801	−0.23204
$C_{2s,2}$	−0.21001	−0.20133	−0.20016	−0.21460	−0.22715	−0.17324
$C_{2s,3}$	0.07593	0.06997	0.06934	0.08022	0.07179	0.02477
$C_{2s,4}$	0.17263	0.17368	0.17136	0.20563	0.13283	0.17350
$C_{2s,5}$	0.90099	0.89900	0.90007	0.86777	0.94252	0.90538
$C_{2s,6}$	0.00586	0.00558	0.00719	0.00543	0.02443	0.00693
$C_{2s,7}$	−0.00023	−0.00015	0.00006	0.00042	0.00979	−0.00024
ϵ_{3s}	−0.73320	−1.07288	−1.17570	−1.22317	−1.20787	−1.23087
Cusp	−16.96224	−16.94416	−16.94540	−16.97671	−17.00251	−16.98601
$C_{3s,1}$	0.06317	0.06541	0.06693	0.07000	0.07341	0.07252
$C_{3s,2}$	0.07620	0.07656	0.07770	0.09087	0.09926	0.07018
$C_{3s,3}$	−0.02132	−0.02034	−0.02053	−0.02158	−0.02157	−0.00184
$C_{3s,4}$	−0.00604	−0.00017	−0.00059	0.01419	0.03314	0.02248
$C_{3s,5}$	−0.40771	−0.42851	−0.43667	−0.49099	−0.52027	−0.48357
$C_{3s,6}$	0.70755	0.65176	0.68652	0.64384	0.67449	0.64311
$C_{3s,7}$	0.43093	0.48089	0.44414	0.51051	0.46565	0.50431
ϵ_{2p}	−7.69557	−8.07218	−8.14619	−9.00679	−8.78960	−9.55946
Cusp	−8.44006	−8.43660	−8.44048	−8.44624	−8.47497	−8.51969
$C_{2p,1}$	0.01990	0.01930	0.01875	0.01324	0.01236	0.00767
$C_{2p,2}$	0.68564	0.68305	0.68657	0.66057	0.65222	0.63922
$C_{2p,3}$	0.19201	0.19262	0.18707	0.22510	0.23727	0.24850
$C_{2p,4}$	0.16481	0.16636	0.17024	0.14711	0.15609	0.15979
$C_{2p,5}$	0.00296	0.00516	0.00323	0.01950	0.00104	0.00535
$C_{2p,6}$	−0.00058	−0.00107	−0.00129	0.01128	0.00016	−0.00209
$C_{2p,7}$	0.00024	0.00111	0.00063	0.00531	0.00000	0.00100
ϵ_{3p}	−0.15017	−0.50640	−0.50063	−0.58967	−0.58465	−0.59605
Cusp	−8.38032	−8.35998	−8.35630	−8.38535	−8.37179	−8.40151
$C_{3p,1}$	−0.00350	−0.00346	−0.00331	−0.00274	−0.00199	−0.00022
$C_{3p,2}$	−0.18172	−0.19968	−0.20013	−0.22358	−0.20251	−0.19667
$C_{3p,3}$	−0.03172	−0.02837	−0.02733	−0.05978	−0.05454	−0.04580
$C_{3p,4}$	−0.06118	−0.07143	−0.07165	−0.07294	−0.07260	−0.07354
$C_{3p,5}$	0.59454	0.60295	0.62287	0.63710	0.63463	0.63029
$C_{3p,6}$	0.36833	0.31482	0.33734	0.32628	0.32834	0.33878
$C_{3p,7}$	0.21232	0.21687	0.17781	0.18060	0.18278	0.17251

[a] States which are not the lowest of a symmetry species.

Table IV. SCF orbitals and energies for Ar and *nl*-hole states of Ar, accurate basis sets.

	Ar(^1S)	Ar$^+$(^2P) 3*p* hole	Ar$^+$(^2S) 3*s* hole	Ar$^+$(^2P) [a] 2*p* hole	Ar$^+$(^2S) [a] 2*s* hole	Ar$^+$(^2S) [a] 1*s* hole
E	−526.8175	−526.2745	−525.5977	−517.6690	−514.8795	−409.3890
V/T	−2.000000	−1.999999	−1.999999	−1.999999	−2.000001	−2.000000
$\zeta_1(1s)$	20.750	20.750	20.735	20.700	20.615	20.080
$\zeta_2(2s)$	14.900	14.900	14.900	14.945	15.000	16.845
$\zeta_3(3s)$	16.500	16.500	16.500	16.500	16.500	18.500
$\zeta_4(3s)$	10.500	10.584	10.758	10.628	10.543	10.863
$\zeta_5(2s)$	6.206	6.224	6.253	6.451	6.498	6.544
$\zeta_6(3s)$	3.166	3.259	3.232	3.458	3.382	3.532
$\zeta_7(3s)$	1.993	2.185	2.201	2.311	2.278	2.340
$\zeta_1(2p)$	16.220	16.160	16.195	17.020	17.460	17.720
$\zeta_2(2p)$	8.230	8.180	8.200	8.410	8.500	9.055
$\zeta_3(2p)$	5.000	4.795	4.865	5.000	5.115	5.450
$\zeta_4(4p)$	8.000	8.000	8.000	8.500	8.500	8.900
$\zeta_5(3p)$	2.970	2.955	2.976	3.157	3.159	3.214
$\zeta_6(4p)$	2.211	2.209	2.242	2.359	2.358	2.385
$\zeta_7(3p)$	1.370	1.550	1.550	1.620	1.620	1.650
ϵ_{1s}	−118.61014	−119.13309	−119.19462	−120.65776	−120.39576	−127.27956
Cusp	−18.00366	−18.00349	−18.00287	−18.00005	−18.00218	−18.00163
$C_{1s,1}$	0.78751	0.78752	0.78834	0.79073	0.79512	0.83865
$C_{1s,2}$	0.41319	0.41322	0.41103	0.40339	0.38653	0.23192
$C_{1s,3}$	−0.17634	−0.17640	−0.17492	−0.17014	−0.15765	−0.05294
$C_{1s,4}$	−0.00008	−0.00004	−0.00022	0.00027	0.00121	0.00265
$C_{1s,5}$	−0.00011	−0.00016	−0.00006	−0.00047	−0.00020	0.01419
$C_{1s,6}$	0.00007	0.00011	0.00006	0.00009	0.00011	−0.00213
$C_{1s,7}$	−0.00006	−0.00008	−0.00008	−0.00008	−0.00008	−0.00203
ϵ_{2s}	−12.32193	−12.83568	−12.88311	−13.61576	−13.77370	−14.17473
Cusp	−17.99649	−18.00356	−18.01242	−18.01453	−18.02974	−17.95176
$C_{2s,1}$	−0.22353	−0.22365	−0.22356	−0.22847	−0.22912	−0.25356
$C_{2s,2}$	−0.21917	−0.22087	−0.22339	−0.23284	−0.22911	−0.15950
$C_{2s,3}$	0.08753	0.08586	0.08258	0.08007	0.07458	0.02281
$C_{2s,4}$	0.16903	0.16072	0.14166	0.13434	0.11753	0.15781
$C_{2s,5}$	0.90732	0.91795	0.93996	0.95521	0.96271	0.92791
$C_{2s,6}$	0.00708	0.00704	0.00956	0.00977	0.02490	0.00833
$C_{2s,7}$	−0.00043	−0.00048	−0.00049	−0.00085	0.00965	−0.00047
ϵ_{3s}	−1.27725	−1.71114	−1.81793	−1.89228	−1.87409	−1.90809
Cusp	−17.96890	−17.94414	−17.92541	−17.97576	−18.00103	−17.96324
$C_{3s,1}$	0.06982	0.07189	0.07327	0.07702	0.08092	0.08360
$C_{3s,2}$	0.08792	0.09287	0.09574	0.10727	0.11101	0.07415
$C_{3s,3}$	−0.02628	−0.02782	−0.02893	−0.02530	−0.02355	−0.00188
$C_{3s,4}$	0.00341	0.01304	0.01863	0.04101	0.05414	0.03755
$C_{3s,5}$	−0.45394	−0.48178	−0.49483	−0.55249	−0.58015	−0.53655
$C_{3s,6}$	0.66908	0.60576	0.63355	0.60842	0.62943	0.59459
$C_{3s,7}$	0.46963	0.53030	0.50098	0.54305	0.51521	0.55658
ϵ_{2p}	−9.57127	−10.08324	−10.14966	−11.10837	−10.86746	−11.71786
Cusp	−8.92591	−8.91125	−8.91441	−8.92308	−8.96769	−8.98739
$C_{2p,1}$	0.01876	0.01845	0.01832	0.01284	0.01174	0.00570
$C_{2p,2}$	0.63009	0.66020	0.65271	0.64006	0.61717	0.59627
$C_{2p,3}$	0.27207	0.23154	0.24110	0.25810	0.29030	0.30855
$C_{2p,4}$	0.13409	0.14874	0.14644	0.13301	0.13460	0.14165
$C_{2p,5}$	0.00309	0.00086	0.00001	0.01590	−0.00093	0.00252
$C_{2p,6}$	−0.00058	0.00171	0.00061	0.01386	0.00165	−0.00075
$C_{2p,7}$	0.00028	−0.00037	−0.00031	0.00155	−0.00088	0.00047
ϵ_{3p}	−0.59092	−1.04532	−1.03104	−1.15880	−1.15303	−1.17532
Cusp	−8.88089	−8.88838	−8.86398	−8.89927	−8.89853	−8.93455
$C_{3p,1}$	−0.00346	−0.00391	−0.00345	−0.00290	−0.00204	0.00005
$C_{3p,2}$	−0.18973	−0.20843	−0.21009	−0.22991	−0.20638	−0.19549
$C_{3p,3}$	−0.06049	−0.06140	−0.05246	−0.08803	−0.08549	−0.08377
$C_{3p,4}$	−0.06178	−0.06560	−0.07057	−0.06915	−0.06887	−0.06753
$C_{3p,5}$	0.60487	0.66790	0.65321	0.68195	0.68125	0.68076
$C_{3p,6}$	0.30887	0.33443	0.32329	0.33574	0.33983	0.33549
$C_{3p,7}$	0.22836	0.12476	0.14980	0.11967	0.11682	0.11520

[a] States which are not the lowest of a symmetry species.

TABLE V. SCF orbitals and energies for K^{+} and nl-hole states of K^{+}, accurate basis sets.

	$\mathrm{K}^{+}(^{1}S)$	$\mathrm{K}^{++}(^{2}P)$ 3p hole	$\mathrm{K}^{++}(^{2}S)$ 3s hole	$\mathrm{K}^{++}(^{2}P)$ [a] 2p hole	$\mathrm{K}^{++}(^{2}S)$ [a] 2s hole	$\mathrm{K}^{++}(^{2}S)$ [a] 1s hole
E	−599.0175	−597.8915	−597.1039	−587.6833	−584.6720	−466.4285
V/T	−1.999999	−2.000000	−1.999999	−2.000000	−2.000002	−1.999997
$\zeta_1(1s)$	21.530	21.545	21.685	21.480	21.300	20.400
$\zeta_2(2s)$	15.255	15.220	15.095	15.300	15.400	17.200
$\zeta_3(3s)$	17.000	17.000	17.000	17.000	17.000	19.000
$\zeta_4(3s)$	11.085	11.258	11.323	10.957	11.262	11.560
$\zeta_5(2s)$	6.687	6.724	6.711	6.878	7.010	7.025
$\zeta_6(3s)$	3.502	3.520	3.599	3.787	3.660	3.814
$\zeta_7(3s)$	2.338	2.491	2.573	2.658	2.600	2.662
$\zeta_1(2p)$	17.000	17.000	17.020	17.800	18.460	20.000
$\zeta_2(2p)$	8.890	8.820	8.855	9.075	9.210	9.920
$\zeta_3(2p)$	5.450	5.260	5.315	5.610	5.712	6.100
$\zeta_4(4p)$	8.800	8.800	8.800	9.300	9.300	9.800
$\zeta_5(3p)$	3.253	3.358	3.371	3.562	3.563	3.546
$\zeta_6(4p)$	2.412	...	...	...	...	2.726
$\zeta_7(3p)$	1.650	2.182	2.173	2.294	2.295	2.000
ϵ_1	−133.75212	−134.40390	−134.45519	−136.06387	−135.76859	−143.07622
Cusp	−19.00074	−19.00027	−19.00610	−18.99684	−18.99330	−19.00584
$C_{1s,1}$	0.80888	0.80805	0.80027	0.81209	0.82183	0.88850
$C_{1s,2}$	0.38950	0.39410	0.42346	0.37982	0.34675	0.15967
$C_{1s,3}$	−0.17686	−0.18025	−0.20056	−0.17085	−0.14743	−0.03669
$C_{1s,4}$	−0.00081	−0.00177	−0.00439	−0.00043	−0.00018	0.00249
$C_{1s,5}$	−0.00024	0.00010	0.00074	−0.00055	0.00047	0.01358
$C_{1s,6}$	0.00011	0.00008	0.00001	0.00013	−0.00003	−0.00199
$C_{1s,7}$	−0.00009	−0.00008	−0.00007	−0.00011	−0.00002	−0.00208
ϵ_2	−14.70798	−15.33970	−15.37648	−16.18376	−16.34603	−16.79208
Cusp	−19.00163	−19.00951	−19.01782	−19.00269	−19.03162	−18.95758
$C_{2s,1}$	−0.23231	−0.23224	−0.22961	−0.23712	−0.23933	−0.27074
$C_{2s,2}$	−0.22932	−0.23548	−0.24544	−0.23674	−0.23878	−0.15189
$C_{2s,3}$	0.09750	0.09623	0.10267	0.09486	0.07919	0.02290
$C_{2s,4}$	0.15704	0.14080	0.14292	0.15644	0.09227	0.14450
$C_{2s,5}$	0.92363	0.94521	0.94423	0.93077	0.99761	0.94824
$C_{2s,6}$	0.00901	0.00953	0.01023	0.01075	0.02701	0.00953
$C_{2s,7}$	−0.00103	−0.00166	−0.00050	−0.00133	0.00777	−0.00100
ϵ_3	−1.96377	−2.47767	−2.58881	−2.68728	−2.66588	−2.71203
Cusp	−18.97447	−18.95978	−18.92907	−19.01150	−19.00299	−18.96578
$C_{3s,1}$	0.07649	0.07862	0.07904	0.08360	0.08803	0.09344
$C_{3s,2}$	0.10123	0.10710	0.11452	0.11897	0.12444	0.07854
$C_{3s,3}$	−0.03137	−0.03343	−0.03861	−0.02901	−0.02732	−0.00258
$C_{3s,4}$	0.01616	0.02255	0.02791	0.04360	0.06713	0.04315
$C_{3s,5}$	−0.50319	−0.52525	−0.54237	−0.59121	−0.62553	−0.57324
$C_{3s,6}$	0.63772	0.62378	0.57022	0.57719	0.62575	0.58974
$C_{3s,7}$	0.50386	0.51400	0.57145	0.58011	0.52008	0.56280
ϵ_{2p}	−11.73810	−12.36843	−12.42720	−13.48122	−13.21615	−14.14872
Cusp	−9.40153	−9.40961	−9.39849	−9.42043	−9.45892	−9.47034
$C_{2p,1}$	0.01736	0.01746	0.01681	0.01262	0.01054	0.00253
$C_{2p,2}$	0.60440	0.63378	0.62810	0.59657	0.57059	0.52985
$C_{2p,3}$	0.30758	0.27199	0.27634	0.31579	0.35027	0.39164
$C_{2p,4}$	0.12274	0.13211	0.13435	0.11239	0.11647	0.12198
$C_{2p,5}$	0.00147	−0.00149	−0.00177	0.01286	0.00072	0.00433
$C_{2p,6}$	0.00039	...	...	...	...	−0.00201
$C_{2p,7}$	−0.00023	0.00228	0.00077	0.01746	0.00040	0.00129
ϵ_{3p}	−1.17047	−1.71131	−1.68867	−1.85275	−1.84608	−1.88069
Cusp	−9.40818	−9.41311	−9.39637	−9.43034	−9.42898	−9.41764
$C_{3p,1}$	−0.00387	−0.00406	−0.00374	−0.00323	−0.00207	0.00057
$C_{3p,2}$	−0.19057	−0.21305	−0.21027	−0.22120	−0.19844	−0.18219
$C_{3p,3}$	−0.09892	−0.09160	−0.09122	−0.13117	−0.12730	−0.12897
$C_{3p,4}$	−0.05412	−0.06176	−0.06274	−0.06004	−0.06202	−0.06243
$C_{3p,5}$	0.67017	0.52926	0.52899	0.54360	0.54095	0.69616
$C_{3p,6}$	0.34285	...	...	...	...	0.32599
$C_{3p,7}$	0.12328	0.57550	0.57691	0.57136	0.57394	0.10617

[a] States which are not the lowest of a symmetry species.

These techniques are described in more detail elsewhere.[8,15] The calculations were performed using computer programs written for the IBM 704 and 7090/4 by Professor C. C. J. Roothaan and the author,[3] with the assistance of various members of the Laboratory of Molecular Structure and Spectra at the University of Chicago. The programs are available for distribution upon request.

IV. RESULTS AND DISCUSSION OF THE SCF CALCULATIONS

A. The SCF Wave Functions

The most accurate SCF wave functions that were obtained for each state are given in Tables II–V. Somewhat less accurate, but still quite useful, SCF wave functions computed with smaller basis sets are presented elsewhere.[15] The results in Tables II–V include the total energy for the usual nonrelativistic fixed nucleus Hamiltonian and the virial coefficient V/T. Exponents of the basis functions are given for each state. The principal quantum number and symmetry type of each basis function is given in parenthesis in the first column of each table. The different basis functions are numbered consecutively within each symmetry type. For each orbital, the SCF orbital energy ϵ_{nl}, the cusp, and the expansion coefficients $C_{nl,p}$ are given. The numbering of the expansion coefficients corresponds to the numbering of the basis functions. All energies are given in Hartrees (1 Hartree$=$27.2098 eV). The results reported in Tables II–V are from calculations performed on an IBM 7094.

The cusp condition, satisfied by exact solutions of the HF equations, is given by

$$[(1/f_{nl})(df_{nl}/dr)]_{r=0}=-Z/(l+1)\,, \qquad (4)$$

where $r^l f_{nl}(r)=r^{-1}P_{nl}(r)$ is the radial part of the orbital. The cusp value may be used as a criterion of the accuracy near the origin of an expansion SCF orbital. The virial theorem,

$$V/T=\langle\Psi|\mathcal{V}|\Psi\rangle/\langle\Psi|\mathcal{T}|\Psi\rangle=-2\,, \qquad (5)$$

where $\mathcal{V}$ and $\mathcal{T}$ are the many-electron potential- and kinetic-energy operators, is satisfied for exact HF wave functions, and for expansion SCF wave functions when the values of the exponents of the basis functions, as well the expansion coefficients $C_{nl,p}$, satisfy variational equations. The virial theorem is a necessary but by no means a sufficient condition that optimum values of the exponents have been used. Discussions of the usefulness of these criteria of the accuracy of expansion SCF wave functions are given elsewhere.[8,15]

The total wave functions for the states given in Tables II–V are all single determinants. The ^1S and ^2S states have even parity and the ^2P states have odd parity. The parity follows immediately from the electron configurations of the states.

The 1*s*-hole states of F^-, Ne, and Na^+ and the 1*s*-, 2*s*-, and 2*p*-hole states of Cl^-, Ar, and K^+ are not the lowest states of their symmetry species; these states are marked with an asterisk in Tables II–V.

The 2*s*-hole states of Ne and Na^+ and the 3*s*-hole states of Ar and K^+ are the first excited states of Ne^+, Na^{++}, Ar^+, and K^{++}, respectively; they are the lowest ^2S states of these systems. It seems reasonable that the 2*s*-hole state of F^- and the 3*s*-hole state of Cl^- are the lowest ^2S states of even parity of F and Cl, respectively. The 2*s*-hole state of F^- is a highly excited state of F; it is, in fact, past the ionization limit. However, Moore[16] does not give any other ^2S state of even parity in the spectrum of F. According to Moore,[16] the 3*s*-hole state of Cl^- is not observed, but, then, no ^2S states of even parity are observed in the spectrum of Cl.

The importance of having reliable estimates of the accuracy of *expansion* SCF wave functions should be stressed. By accuracy of the expansion SCF wave functions we mean how closely they represent the exact solutions of the HF equations. Techniques for determining this accuracy have been developed and are described in detail elsewhere.[8,15] Using these techniques, we have made estimates of the accuracy of the SCF functions given in Tables II–V.[15] These estimates are based largely on a very careful analysis of the accuracy of the SCF wave functions for F^-, Ne, Cl^-, and Ar. They are generous and probably indicate, for most of the functions, errors larger than the true errors.

The SCF total energy E_{SCF} represents the exact HF total energy to within 2 units in the 7th significant figure, and the orbital energies ϵ_{nl} are accurate to about 5 units in the same place past the decimal that the error enters into E_{SCF}. When E_{SCF} is <100, the ϵ_{nl} are accurate to 5 units in the 5th place past the decimal and when E_{SCF} is $\geqslant 100$, to 5 units in the 4th place past the decimal.

To describe the error of the SCF orbitals we give the error of the radial functions $P_{nl}(r)$. [$P_{nl}(r)$ is r times the radial part of the orbital.] For the states of the heavier atoms (Cl, Ar, and K) the 1*s*, 2*s*, and 2*p* radial functions do not differ from the exact HF solutions, for any value of r, by more than 0.0005. The 1*s* radial function is probably accurate to within 0.0002. The 3*s* and 3*p* radial functions are accurate to within 0.0015 and over much of the range of r are accurate to within 0.0005. The only exception is the 3*s* radial function of Cl^-, for which the error is as large as 0.0025 for a fairly small range of r near the tail of the function. For the states of the light atoms (F, Ne, and Na) the 1*s* radial function is accurate to within 0.0002 and the 2*s* and 2*p* radial

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[15] P. S. Bagus, Argonne National Laboratory Technical Report ANL 6959, 1964 (unpublished). Copies of this report may be obtained from Argonne National Laboratory or the U. S. Office of Technical Services, Department of Commerce, Washington 25, D. C.

[16] C. E. Moore, Nat. Bur. Std. (U. S.) Circ. 467 (1949), Vol. I, and corrections in Vol. II (1952) and Vol. III (1958).

functions to within 0.0005. The radial function of the outermost s shell ($2s$ for the light atoms and $3s$ for the heavier atoms) is the least accurate function for a given state. The outermost s shell makes the smallest contribution to the total energy and so is least well determined by the exponent variation procedures which minimize the total energy.

Although the vectors (of expansion coefficients) given in Tables II–V are not representations of the exact HF orbitals to the number of figures given, they do form an orthonormal set to the number of figures given.

The SCF wave functions given, except for the functions for Cl^- and the $1s$-hole state of K^+, are the most accurate functions which can be obtained using the single precision, eight significant figure, floating point arithmetic of the IBM 7094 computer. The Cl^- function could probably be improved with the addition of an s and possibly a p basis function to the basis set. The function for the $1s$-hole state of K^+ could be improved very slightly if the arithmetic of the exponent variation procedures were changed to minimize roundoff error. (This change has already been made in the latest versions of the SCF programs.)

Expectation values of r and r^2, in atomic units (1 Bohr=0.52917 Å), for all the states computed are given in Tables VI and VII. For each state, the expectation values of r and r^2 taken with respect to each occupied orbital, $\langle r\rangle_{nl}=\int_0^\infty [P_{nl}(r)]^2 r dr$ and $\langle r^2\rangle_{nl}=\int_0^\infty [P_{nl}(r)]^2 r^2 dr$, are given. The average values of $\langle r\rangle$ and $\langle r^2\rangle$ are also given. The average value of $\langle r\rangle$ is defined by $\sum N_{nl}\langle r\rangle_{nl}/\sum N_{nl}$, where N_{nl} is the electron occupation of the nl orbital and the sum is over all occupied orbitals. The values of $\langle r\rangle_{nl}$ and $\langle r^2\rangle_{nl}$ represent the exact HF values to within a few units in the last figure given. The values of $\langle r^2\rangle_{nl}$ for the outermost s and p orbitals of each state are the least accurate and the error for these values may be as large as 20 units in the last figure.

TABLE VI. Expectation values of r and r^2 for F^-, Ne, and Na^+ and nl-hole states of F^-, Ne, and Na^+.

	$\mathrm{F}^-(^1S)$	$\mathrm{F}(^2P)$ $2p$ hole	$\mathrm{F}(^2S)$ $2s$ hole	$\mathrm{F}(^2S)$ $1s$ hole
$\langle r\rangle_{1s}$	0.1758	0.1757	0.1760	0.1718
$\langle r\rangle_{2s}$	1.0355	1.0011	0.9885	0.9435
$\langle r\rangle_{2p}$	1.2556	1.0847	1.0934	0.9659
$\sum N_i\langle r\rangle_i/\sum N_i$	0.99560	0.86411	0.87790	0.87267
$\langle r^2\rangle_{1s}$	0.04162	0.04161	0.04177	0.04045
$\langle r^2\rangle_{2s}$	1.3189	1.2164	1.1827	1.0836
$\langle r^2\rangle_{2p}$	2.2096	1.5429	1.5738	1.2245
$\sum N_i\langle r^2\rangle_i/\sum N_i$	1.59783	1.13672	1.18988	1.06166
	$\mathrm{Ne}(^1S)$	$\mathrm{Ne}^+(^2P)$ $2p$ hole	$\mathrm{Ne}^+(^2S)$ $2s$ hole	$\mathrm{Ne}^+(^2S)$ $1s$ hole
$\langle r\rangle_{1s}$	0.1576	0.1576	0.1578	0.1545
$\langle r\rangle_{2s}$	0.8921	0.8603	0.8536	0.8171
$\langle r\rangle_{2p}$	0.9652	0.8759	0.8841	0.7993
$\sum N_i\langle r\rangle_i/\sum N_i$	0.78905	0.71280	0.71931	0.73159
$\langle r^2\rangle_{1s}$	0.03347	0.03344	0.03357	0.03260
$\langle r^2\rangle_{2s}$	0.9669	0.8903	0.8751	0.8056
$\langle r^2\rangle_{2p}$	1.2279	0.9820	1.0032	0.8196
$\sum N_i\langle r^2\rangle_i/\sum N_i$	0.93682	0.75081	0.77351	0.72903
	$\mathrm{Na}^+(^1S)$	$\mathrm{Na}^{++}(^2P)$ $2p$ hole	$\mathrm{Na}^{++}(^2S)$ $2s$ hole	$\mathrm{Na}^{++}(^2S)$ $1s$ hole
$\langle r\rangle_{1s}$	0.1429	0.1428	0.1430	0.1403
$\langle r\rangle_{2s}$	0.7791	0.7530	0.7491	0.7196
$\langle r\rangle_{2p}$	0.7962	0.7385	0.7453	0.6845
$\sum N_i\langle r\rangle_i/\sum N_i$	0.66214	0.60932	0.61190	0.63182
$\langle r^2\rangle_{1s}$	0.02748	0.02744	0.02755	0.02681
$\langle r^2\rangle_{2s}$	0.7314	0.6779	0.6703	0.6210
$\langle r^2\rangle_{2p}$	0.8159	0.6889	0.7033	0.5932
$\sum N_i\langle r^2\rangle_i/\sum N_i$	0.64130	0.53945	0.54949	0.53645

TABLE VII. Expectation values of r and r^2 for Cl^-, Ar, and K^+ and nl-hole states of Cl^-, Ar, and K^+.

	$\mathrm{Cl}^-(^1S)$	$\mathrm{Cl}(^2P)$ $3p$ hole	$\mathrm{Cl}(^2S)$ $3s$ hole	$\mathrm{Cl}(^2P)$ $2p$ hole	$\mathrm{Cl}(^2S)$ $2s$ hole	$\mathrm{Cl}(^2S)$ $1s$ hole
$\langle r\rangle_{1s}$	0.09130	0.09130	0.09130	0.09121	0.09134	0.09031
$\langle r\rangle_{2s}$	0.4418	0.4417	0.4424	0.4338	0.4390	0.4226
$\langle r\rangle_{3s}$	1.6018	1.5557	1.5341	1.4696	1.4759	1.4514
$\langle r\rangle_{2p}$	0.4054	0.4057	0.4050	0.4004	0.3952	0.3776
$\langle r\rangle_{3p}$	2.0288	1.8418	1.8380	1.6928	1.6992	1.6623
$\sum N_i\langle r\rangle_i/\sum N_i$	1.04860	0.93065	0.94469	0.94988	0.94942	0.94573
$\langle r^2\rangle_{1s}$	0.01120	0.01120	0.01120	0.01117	0.01122	0.01105
$\langle r^2\rangle_{2s}$	0.2313	0.2312	0.2321	0.2225	0.2300	0.2117
$\langle r^2\rangle_{3s}$	3.0104	2.8131	2.7299	2.5069	2.5364	2.4472
$\langle r^2\rangle_{2p}$	0.2039	0.2043	0.2034	0.2020	0.1930	0.1762
$\langle r^2\rangle_{3p}$	5.1081	4.0575	4.0444	3.4404	3.4480	3.3052
$\sum N_i\langle r^2\rangle_i/\sum N_i$	2.13207	1.62498	1.68842	1.59608	1.59830	1.54220
	$\mathrm{Ar}(^1S)$	$\mathrm{Ar}^+(^2P)$ $3p$ hole	$\mathrm{Ar}^+(^2S)$ $3s$ hole	$\mathrm{Ar}^+(^2P)$ $2p$ hole	$\mathrm{Ar}^+(^2S)$ $2s$ hole	$\mathrm{Ar}^+(^2S)$ $1s$ hole
$\langle r\rangle_{1s}$	0.08610	0.08610	0.08611	0.08602	0.08614	0.08523
$\langle r\rangle_{2s}$	0.4123	0.4121	0.4128	0.4052	0.4100	0.3954
$\langle r\rangle_{3s}$	1.4220	1.3814	1.3679	1.3162	1.3209	1.3005
$\langle r\rangle_{2p}$	0.3753	0.3756	0.3749	0.3714	0.3667	0.3515
$\langle r\rangle_{3p}$	1.6628	1.5584	1.5589	1.4560	1.4627	1.4321
$\sum N_i\langle r\rangle_i/\sum N_i$	0.89274	0.81205	0.82171	0.83576	0.83531	0.83403
$\langle r^2\rangle_{1s}$	0.00996	0.00996	0.00996	0.00994	0.00997	0.00983
$\langle r^2\rangle_{2s}$	0.2012	0.2010	0.2019	0.1940	0.2003	0.1852
$\langle r^2\rangle_{3s}$	2.3491	2.2018	2.1570	1.9980	2.0185	1.9517
$\langle r^2\rangle_{2p}$	0.1743	0.1747	0.1739	0.1730	0.1658	0.1524
$\langle r^2\rangle_{3p}$	3.3092	2.8601	2.8642	2.5102	2.5196	2.4179
$\sum N_i\langle r^2\rangle_i/\sum N_i$	1.44565	1.18672	1.22406	1.19586	1.19821	1.15911
	$\mathrm{K}^+(^1S)$	$\mathrm{K}^{++}(^2P)$ $3p$ hole	$\mathrm{K}^{++}(^2S)$ $3s$ hole	$\mathrm{K}^{++}(^2P)$ $2p$ hole	$\mathrm{K}^{++}(^2S)$ $2s$ hole	$\mathrm{K}^{++}(^2S)$ $1s$ hole
$\langle r\rangle_{1s}$	0.08147	0.08146	0.08147	0.08139	0.08150	0.08069
$\langle r\rangle_{2s}$	0.3864	0.3861	0.3869	0.3801	0.3845	0.3715
$\langle r\rangle_{3s}$	1.2768	1.2435	1.2341	1.1922	1.1959	1.1787
$\langle r\rangle_{2p}$	0.3494	0.3496	0.3490	0.3462	0.3419	0.3287
$\langle r\rangle_{3p}$	1.4312	1.3611	1.3629	1.2850	1.2915	1.2657
$\sum N_i\langle r\rangle_i/\sum N_i$	0.78740	0.72503	0.73189	0.74991	0.74942	0.74987
$\langle r^2\rangle_{1s}$	0.00891	0.00891	0.00891	0.00889	0.00892	0.00880
$\langle r^2\rangle_{2s}$	0.1766	0.1763	0.1771	0.1706	0.1759	0.1634
$\langle r^2\rangle_{3s}$	1.8818	1.7761	1.7481	1.6320	1.6477	1.5962
$\langle r^2\rangle_{2p}$	0.1508	0.1511	0.1504	0.1497	0.1439	0.1330
$\langle r^2\rangle_{3p}$	2.4161	2.1646	2.1712	1.9402	1.9497	1.8741
$\sum N_i\langle r^2\rangle_i/\sum N_i$	1.08532	0.92071	0.94407	0.94193	0.94416	0.91592

B. Validity of the Exponent Variation Procedure for Excited States

The basis function exponent variation procedure selects values of the exponents which minimize the SCF total energy. For a state which is not the lowest of a symmetry species, exponents chosen to minimize the total energy may not give an SCF wave function which is an optimum representation of the exact HF solution.

TABLE VIII. Comparison of SCF and experimental ionization potentials for the *nl*-hole states of F^-, Ne, Na^+, Cl^-, Ar, and K^+ (Energies in Hartrees, 1 Hartree = 27.2098 eV = 2.19475×10^5 cm^{-1}).

State				IP(exp) [a]	IP(nr) [a]	IP($-\epsilon_{nl}$)	ΔIP($-\epsilon_{nl}$) [b]	IP(ΔE_{SCF})	ΔIP(ΔE_{SCF}) [b]
$2p$ hole	$1s^22s^2\mathbf{2p^6}$	$F^{-\,c,d}$		0.1273	···	0.1810	−0.0537 (−1.461 eV)	0.0501	+0.0772 (+2.101 eV)
		Ne^d		0.7937	···	0.8503	−0.0566 (−1.540 eV)	0.7293	+0.0644 (+1.752 eV)
		$Na^{+\,d}$		1.7405	···	1.7972	−0.0567 (−1.543 eV)	1.6796	+0.0609 (+1.657 eV)
$2s$ hole	$1s^2\mathbf{2s}2p^6$	$F^{-\,c,d}$		0.8947	···	1.0746	−0.1799 (−4.895 eV)	0.9282	−0.0335 (−0.912 eV)
		Ne ^{d}		1.7815	···	1.9303	−0.1488 (−4.049 eV)	1.8123	−0.0308 (−0.838 eV)
		$Na^{+\,d}$		2.9434	···	3.0737	−0.1303 (−3.545 eV)	2.9682	−0.0248 (−0.675 eV)
$1s$ hole	$\mathbf{1s}2s^22p^6$	$F^{-\,e}$		24.99_2	24.96_7	25.8296	-0.86_3 ($-23._{48}$ eV)	24.9353	$+0.03_2$ ($+0.8_7$ eV)
		Ne ^{e}		31.98_5	31.94_5	32.7723	-0.82_7 ($-22._{50}$ eV)	31.9214	$+0.02_4$ ($+0.6_5$ eV)
		$Na^{+\,e}$		40.00_0	39.93_8	40.7597	-0.82_2 ($-22._{37}$ eV)	39.9345	$+0.00_3$ ($+0.0_8$ eV)
$3p$ hole	$1s^22s^22p^63s^2\mathbf{3p^5}$	$Cl^{-\,c,d}$		0.1341	···	0.1502	−0.0161 (−0.438 eV)	0.0948	+0.0393 (+1.069 eV)
		Ar ^{d}		0.5813	···	0.5909	−0.0096 (−0.261 eV)	0.5430	+0.0383 (+1.042 eV)
		$K^{+\,d}$		1.1726	···	1.1705	+0.0021 (+0.057 eV)	1.1260	+0.0466 (+1.268 eV)
$3s$ hole	$1s^22s^22p^6\mathbf{3s}3p^6$	$Cl^{-\,c,f}$		0.52_6(?)	···	0.7332	-0.20_7 (-5.6_3 eV)	0.6601	-0.13_4 (-3.6_5 eV)
		Ar ^{d}		1.0745	···	1.2773	−0.2028 (−5.518 eV)	1.2198	−0.1453 (−3.954 eV)
		$K^{+\,d}$		1.7644	···	1.9638	−0.1994 (−5.426 eV)	1.9136	−0.1492 (−4.060 eV)
$2p$ hole	$1s^22s^2\mathbf{2p^5}3s^23p^6$	$Cl^{-\,e}$	$^2P_{3/2}$ $^2P_{1/2}$	7.22_0 7.27_9	7.22_8	7.6956	-0.46_8 (-12.7_3 eV)	7.2420	-0.01_4 (-0.3_8 eV)
		Ar ^{e}	$^2P_{3/2}$ $^2P_{1/2}$	9.13_3 9.20_9	9.14_2	9.5713	-0.42_9 (-11.6_7 eV)	9.1484	-0.00_6 ($-0._2$ eV)
		$K^{+\,e}$	$^2P_{3/2}$ $^2P_{1/2}$	11.30_6 11.41_6	11.31_5	11.7381	-0.42_3 (-11.5_1 eV)	11.3342	-0.01_9 (-0.5_2 eV)
$2s$ hole	$1s^2\mathbf{2s}2p^63s^23p^6$	$Cl^{-\,g}$		9.7(?)	···	10.2292	···	9.8114	···
		Ar		···	···	12.3219	···	11.9380	···
		$K^{+\,g}$		14.4(?)	···	14.7080	···	14.3455	···
$1s$ hole	$\mathbf{1s}2s^22p^63s^23p^6$	$Cl^{-\,e}$		103.59_9	103.1_8	104.5055	-1.3_3 ($-36._2$ eV)	103.2947	-0.1_1 ($-3._0$ eV)
		Ar ^{e}		117.83_7	117.3_0	118.6101	-1.3_1 ($-35._6$ eV)	117.4284	-0.1_3 ($-3._5$ eV)
		$K^{+\,e}$		133.09_5	132.4_2	133.7521	-1.3_3 ($-36._2$ eV)	132.5890	-0.1_7 ($-4._6$ eV)

[a] IP(exp) is the experimental value of the ionization potential. Unless explicitly indicated otherwise, IP(exp) for ^2P terms is given to the center of gravity of the ^2P term. IP(nr) is obtained by correcting IP(exp) for relativistic effects; for a discussion of these corrections see the text. Both IP(exp) and IP(nr) include a correction to infinite nuclear mass.

[b] When a value of IP(nr) is not given, ΔIP($-\epsilon_{nl}$) is obtained from the relation ΔIP($-\epsilon_{nl}$) = IP(exp) − IP($-\epsilon_{nl}$); otherwise it is ΔIP($-\epsilon_{nl}$) = IP(nr) − IP($-\epsilon_{nl}$). The values of ΔIP(ΔE_{SCF}) are obtained in the same way.

[c] Experimental data for the electron affinities of F^- and Cl^- are from R. S. Berry and C. W. Reimann, J. Chem. Phys. 38, 1540 (1963).

[d] Experimental data from C. E. Moore, see Ref. 16.

[e] Except for the 1*s*-hole IP's of Ar and Ne, the value of IP(exp) is obtained by combining the IP for the removal of an outer shell electron with the energies of x-ray emission lines. For the 1*s*-hole IP's of Ne and Ar, the value of the K absorption edge is used for IP(exp). For sources of the x-ray experimental data see Ref. 15.

[f] IP(exp) is obtained using an estimate of the 3*s*-hole term value of Cl^- made by Rohrlich and reported by Varsavsky; C. M. Varsavsky, Astrophys. J. Suppl. 6, 75 (1961).

[g] IP(exp) is obtained from an interpolation made by Tomboulian and Cady which uses the $L_{I}-L_{II}$ screening doublet splitting rule and the known term value of the L_{II}($2p$ hole, $^2P_{1/2}$) level; see Ref. 25. The values given by Tomboulian and Cady for the L_I level are 19.8 Ry for Cl and 27.7 Ry for K (1 Ry = 0.5 Hartrees). Corrections of −0.3 Ry for Cl^- and +1.1 Ry for K^+ are used to obtain the values of IP(exp) given here. These are the corrections required to bring the term values for the L_{II} level used by Tomboulian and Cady (14.9 Ry for Cl and 21.7 Ry for K) into agreement with the values of IP(exp) for the 2*p*-hole, $^2P_{1/2}$ state given in this Table. This may be regarded as a correction for different zeros of energy used by Tomboulian and Cady and by us.

There is no known theorem from which we may infer that the *expansion* SCF total energy is an upper bound to the exact HF energy for the inner shell hole states considered here. Hence, the validity of the variation procedure for these states requires further consideration.

If explicit variational equations, e.g., those given by Dehn,[14] were solved for the exponents of the basis functions, there would be no difficulty with these excited states. Stationary values of the energy would be found with respect to variation of the exponents as well as the expansion coefficients. Using our exponent variation procedure, we do find, in a brute-force fashion, a particular stationary value of the energy.[3] The stationary value found is, of course, a minimum. This stationary value was found with no more difficulty for the excited states than for the ground states.

It seems unlikely, for an expansion SCF wave function of a particular state, that there will be more than one stationary value of the energy. It is reasonable that the solutions of the variational equations for both the expansion coefficients and the exponents are unique. If this is true, then the use of our exponent variation procedure is justified since we always found a stationary value with respect to variation of the exponents.

The procedure may also be justified from the results of the SCF calculations. The virial theorem, which may be used as an indication of how well the exponents of the basis functions have been optimized, is satisfied equally well for the excited-state wave functions and the ground-state functions. The cusp condition is also satisfied equally well for the excited-state functions and the ground-state functions. Further, as may be seen from Table VIII, the calculated ionization potentials for the removal of an inner shell electron agree quite well with experimental values. The success of our method of exponent variation implies that the total energy of the expansion SCF functions, even for the excited states, is an upper bound to the exact HF energy.

The results in Table VIII also show quite clearly that the SCF energies are, in fact, upper bounds to the exact nonrelativistic total energies. If the SCF total energy of an inner shell hole state was not an upper bound to the exact nonrelativistic energy, then the calculated ionization potential IP(ΔE_{SCF}), obtained by subtracting the SCF energy of the parent from that of the ion, would be much smaller than the true nonrelativistic ionization potential IP(*nr*). It would have to be smaller by at least the magnitude of the correlation energy of the parent closed shell system. According to estimates made by Clementi,[17] this is ~0.4 Hartrees for F^-, Ne, and Na^+, and ~0.8 Hartrees for Cl^-, Ar, and K^+. From the values given in Table VIII, it is clear that the error of IP(ΔE_{SCF}) is not this large.

C. Effect of Off-Diagonal Lagrangian Multipliers

For the open shell states considered here, the off-diagonal Lagrangian multipliers which couple the HF equations for open and closed shell orbitals of the same symmetry cannot be transformed to zero. The off-diagonal Lagrangian multipliers appear in the usual HF equations as inhomogeneous terms[10,18]; i.e.,

$$F\varphi_i=\epsilon_i\varphi_i+\sum_{j\neq i}\theta_{ji}\varphi_j\,, \tag{6}$$

where F includes the one-electron, Coulomb and exchange operators (and is different for closed and open shell orbitals) and the θ_{ji} are the off-diagonal Lagrangian multipliers. Because of the difficulty of handling these inhomogeneous terms, the off-diagonal Lagrangian multipliers are often treated in an approximate way.[19] Roothaan[2,3] has shown that it is possible, through the use of coupling operators, to absorb the terms involving the nonzero off-diagonal multipliers into the HF operator, thus the pseudo-eigenvalue form of the HF equations is preserved. The coupling operator R has the property that for self-consistent solutions of the HF equations $R\varphi_i=\sum_{j\neq i}\theta_{ji}\varphi_j$. The off-diagonal Lagrangian multipliers which appear in the calculations reported herein have been treated without approximation. For the inner shell hole states, the neglect or approximate treatment of the off-diagonal Lagrangian multipliers would significantly affect the results of the SCF calculations.

TABLE IX. Off-diagonal Lagrangian multipliers for the *nl*-hole states of Ar and Ne.[a]

State	Open shell	$\theta_{\text{open shell, closed shell}}$		
		$\theta_{ns,1s}$	$\theta_{ns,2s}$	$\theta_{ns,3s}$
Ar^+(3*s* hole)	3*s*	−0.00136	+0.01046	···
Ar^+(2*s* hole)	2*s*	+0.04518	···	+0.13093
Ar^+(1*s* hole)	1*s*	···	+0.72661	−0.22742
		$\theta_{np,2p}$	$\theta_{np,3p}$	
Ar^+(3*p* hole)	3*p*	+0.01672	···	
Ar^+(2*p* hole)	2*p*	···	+0.24923	
		$\theta_{ns,1s}$	$\theta_{ns,2s}$	
Ne^+(2*s* hole)	2*s*	+0.01644	···	
Ne^+(1*s* hole)	1*s*	···	+0.37522	

[a] The Lagrangian multipliers are not symmetric.

$$\theta_{\text{closed,open}}=(N_c/N_0)\theta_{\text{open,closed}},$$

where N_c and N_0 are the electron occupations of the closed and open shells, respectively.

The values of the nonzero off-diagonal Lagrangian multipliers for the *nl*-hole states of Ar and Ne are given in Table IX. It should be noted that the off-diagonal Lagrangian multipliers are not symmetric; they are related by

$$N_{ml}\theta_{nl,ml}=N_{nl}\theta_{ml,nl}\,, \tag{7}$$

where N_{nl} is the electron occupation of the *nl* shell. While the off-diagonal Lagrangian multipliers are fairly small for states with open outer shells, they are more than an order of magnitude larger for states with open inner shells. The values of the off-diagonal Lagrangian multipliers for the *nl*-hole states of Cl^- and K^+ and F^- and Na^+ are quite similar to the values given for Ar and Ne.

The most striking effect due to the off-diagonal

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[19] R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955); Rev. Mod. Phys. **33**, 28 (1961), and R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 (1961); **124**, 1117 (1961).

TABLE X. Effect of neglecting the off-diagonal Lagrangian multipliers for the *nl*-hole states of Ar and Ne (the results for the correct treatment of the off-diagonal Lagrangian multipliers are denoted by SCF; the results for the approximate treatment by NLM).

State	E(SCF) [a]	E(NLM) [E(SCF)$-E$(NLM)]	V/T(SCF) [a]	V/T(NLM)	Open shell	Overlap integrals between open- and closed-shell orbitals		
						$S_{ns,1s}$	$S_{ns,2s}$	$S_{ns,3s}$
Ar$^+$(3s hole)	-525.5976	-525.5976 [0.0000]	-1.999999	-1.999972	3s	-0.0000_1	$+0.0009_3$	$\cdots$
Ar$^+$(2s hole)	-514.8794	-514.8808 [$+0.0014$]	-2.000000	-2.000242	2s	$+0.0003_9$	$\cdots$	-0.0104_4
Ar$^+$(1s hole)	-409.3890	-409.3941 [$+0.0051$]	-2.000000	-2.001786	1s	$\cdots$	-0.0062_2	$+0.0017_6$
						$S_{np,2p}$	$S_{np,3p}$	
Ar$^+$(3p hole)	-526.2744	-526.2744 [0.0000]	-1.999999	-1.999966	3p	$+0.0003_5$	$\cdots$	
Ar$^+$(2p hole)	-517.6690	-517.6746 [$+0.0056$]	-2.000000	-2.000464	2p	$\cdots$	-0.0043_8	
						$S_{ns,1s}$	$S_{ns,2s}$	
Ne$^+$(2s hole)	-126.7348	-126.7348 [0.0000]	-2.000003	-1.999897	2s	$+0.0005_3$	$\cdots$	
Ne$^+$(1s hole)	-96.62571	-96.62983 [$+0.00412$]	-1.999997	-2.003008	1s	$\cdots$	-0.0102_2	

[a] The results given in this Table are from calculations performed on the IBM 704. Thus E(SCF) and V/T(SCF) may differ slightly from the values of these quantities given in Tables II and IV which are from calculations performed on the IBM 7094.

Lagrangian multipliers is that the 1s orbitals, of the 1s-hole states of Cl$^-$, Ar, and K$^+$ *have a node*. In each of these cases, $P_{1s}(r)$ goes through zero and reaches a minimum value of -0.003. For these 1s-hole states, the HF equation for $P_{1s}(r)$ at large r becomes

$$\epsilon_{1s}P_{1s}(r)\cong-\theta_{2s,1s}P_{2s}(r)-\theta_{3s,1s}P_{3s}(r)\,. \qquad (8)$$

For Ar$^+$ (1s hole), substituting the values given in Tables IV and IX into Eq. (8), we obtain

$$P_{1s}(r)\cong+0.01142P_{2s}(r)-0.00357P_{3s}(r)\,; \qquad (9)$$

the second term on the right is dominant since $P_{2s}(r)$ goes to zero much before $P_{3s}(r)$ does. For $r\gtrsim 1.2$ Bohrs, the values of $P_{1s}(r)$ calculated from Eq. (9), using the values of the SCF radial functions $P_{2s}(r)$ and $P_{3s}(r)$, agree with the values obtained for $P_{1s}(r)$ from the SCF calculation to within 0.00006; the difference is always less than 3%. This is remarkably good agreement, especially since the (finite) expansion SCF orbitals are not exact solutions of the HF integro-differential equations.

With the exception of $\theta_{1s,3s}$ for the 1s-hole and 3s-hole states of Cl$^-$, Ar, and K$^+$, the off-diagonal Lagrangian multipliers are positive. The effect of the positive off-diagonal Lagrangian multipliers is to extend the tails of the inner shell orbitals rather than to introduce additional nodes. The negative value of $\theta_{3s,1s}$ could introduce a node into the 1s orbital of the 3s-hole states. However, the maximum value of $|P_{1s}(r)|$ in the outer loop would be only 0.00001. This is beyond the accuracy of the present calculation and too small to be of any interest. The signs of the off-diagonal Lagrangian multipliers are determined by the sign conventions used for the SCF orbitals. The signs of the orbitals have been chosen so that the 1s, 3s, and 2p radial functions are positive as $r\rightarrow 0$, and the 2s and 3p radial functions are negative as $r\rightarrow 0$.

In order to get further insight into the importance of the off-diagonal Lagrangian multipliers, an approximate treatment was developed in which the off-diagonal Lagrangian multipliers were arbitrarily set equal to zero. (That is, in the notation of Ref. 3, $\mathbf{R}_{0\lambda}$ and $\mathbf{R}_{C\lambda}$ were set equal to zero.) The open-shell orbitals obtained in this way are not orthogonal to the closed-shell orbitals. Therefore, after each iteration, the open-shell orbital was Schmidt orthogonalized to the closed-shell orbitals; this Schmidt orthogonalization does not change the total determinantal wave function. A "self-consistent" solution was obtained when the Schmidt-orthogonalized solutions of these modified HF equations were the same, within convergence thresholds, as the *orthogonal* orbitals that were used to construct the operators. "Self-consistent" solutions obtained in this way are denoted by NLM (Neglect Lagrangian Multipliers) to distinguish them from the SCF solutions obtained from a correct treatment of the off-diagonal Lagrangian multipliers.

NLM calculations were performed, with the same basis sets that were used for the SCF calculations, for the *nl*-hole states of Ar and Ne. The results of these calculations are given in Table X. The NLM calculations were performed on the IBM 704 and are compared with SCF calculations also performed on the 704. [The values of E(SCF) and V/T(SCF) given in Table IX differ slightly, because of round-off, from the values given in Tables II and IV.] Values of the total energy E (in Hartrees), V/T, and the overlap integrals $S_{nl,n'l}$ between the open-shell orbital and the closed-shell orbitals are given. The signs of the $S_{nl,n'l}$ are determined by the sign conventions used for the SCF orbitals.

It is interesting to note, from Table X, that the NLM total energy for a state with an inner shell hole (1*s*, 2*s*, or 2*p* shell of Ar and 1*s* shell of Ne) is lower than the SCF total energy. Unless the trial wave functions for an excited state are constrained to be orthogonal to the *exact* wave functions of all lower lying states, the energy obtained from a solution of variational equations for the excited state is not necessarily the lowest possible energy for that state; the expectation value of the energy for another of the trial functions may very well be lower. Since, as discussed in Sec. II, this orthogonality constraint is not imposed on the determinantal trial functions for the SCF calculation, it should not be surprising that the NLM energies for the inner shell hole states are lower than the corresponding SCF energies. We wish to stress that the NLM energies have been evaluated without approximation for the total wave functions constructed with the NLM orbitals. Although it is tempting to feel that the NLM wave functions for the inner shell hole states are preferable because the NLM energies are lower, this is not the case; the NLM functions are only *approximate* solutions of the Hartree-Fock equations while the SCF functions are correct solutions of these equations. It is quite possible that the reason the NLM energies are lower than the SCF energies is that the NLM functions, when expanded in terms of the exact eigenfunctions, contain a larger contribution of the lower lying eigenfunctions than do the corresponding SCF functions.

The NLM results for states with outer shell holes are almost the same as the SCF results and the $S_{nl,n'l}$ are quite small. However, for the states with inner shell holes, where the off-diagonal Lagrangian multipliers are large, the NLM results are different from the SCF results and the $S_{nl,n'l}$ are an order of magnitude larger than those for the outer shell hole states.

The $S_{nl,n'l}$ are given in order to indicate the deviation of the NLM solutions from the requirement of orthogonality of the orbitals; a requirement imposed in the derivation of the equations. It is important to distinguish between the errors inherent in the one-electron approximation and errors due to the approximate solution of the HF equations, which should, of course, be avoided. For this reason, it is a desirable goal to obtain SCF orbitals which are accurate solutions of the HF equations to three places past the decimal. In terms of such accuracy, a deviation from orthogonality of 0.01 is fairly large.

In order to get further information about the differences between the SCF and NLM solutions, we have also calculated $\langle r \rangle$ and $\langle r^2 \rangle$ for the NLM orbitals of the *nl*-hole states of Ar and Ne. For the outer shell hole states the NLM values of $\langle r \rangle$ and $\langle r^2 \rangle$ are very nearly identical to the SCF values. The largest difference is for $\langle r^2 \rangle_{2p}$ for the 3*p*-hole state of Ar; this difference is only 0.3%. Even for the inner shell hole states, the NLM values of $\langle r \rangle$ and $\langle r^2 \rangle$ are significantly different from the SCF values only for the open-shell orbital (the shell with the electron missing). The error of the NLM value of $\langle r^2 \rangle$, for these cases, is between 3.0% and 5.4% and the error of the NLM value of $\langle r \rangle$ is between 1.0% and 1.9%.

These errors, even those for the inner shell hole states, would not significantly effect the values of properties which depend on $\sum r_i$ or $\sum r_i^2$. However, they do indicate that the errors of the NLM solutions for inner shell hole states are larger than those of the NLM solutions for outer shell hole states.

Further, one may speculate from the errors of $\langle r \rangle$ and $\langle r^2 \rangle$ for inner shell hole states and from the discussion earlier of the introduction of a second node into a 1*s* orbital that the values of properties which are sensitive to the precise shape of the orbitals, e.g., a dipole transition integral between a 1*s* and a 2*p* orbital, may be quite different for NLM and SCF orbitals.

The main purpose of this discussion has been to consider the importance of a correct treatment of the off-diagonal Lagrangian multipliers. It is our feeling that, for states which can be treated with the latest Roothaan open-shell analysis,[3] it is unnecessary to treat the off-diagonal Lagrangian multipliers in an approximate way. The correct treatment, without approximation, of the off-diagonal Lagrangian multipliers is straightforward, uses an extremely small amount of computer time, and *causes no computational difficulties or inconvenience.* This is due to the following facts. Through the use of Roothaan's coupling operators R, the pseudo-eigenvalue form of the HF equations is obtained for open shell, as well as closed shell, systems; thus, the matrix HF equations can be solved using well known and well understood techniques for the solution of matrix eigenvalue problems.[3] The construction of the R operators at each iteration of an SCF calculation is quick and simple. And last, it has been our experience that the R operators do not cause any difficulty in the process of convergence to self-consistency.

V. COMPARISON OF SCF IONIZATION POTENTIALS WITH EXPERIMENT

Experimental data are available for most of the ionization potentials (IP's) of the closed-shell systems considered here. A comparison with experiment of IP's calculated from the SCF wave functions is given in Table VIII. The IP for the removal of an outer shell electron (3*s* or 3*p* shell of the Ar-like ions and 2*s* or 2*p* shell of the Ne-like ions) can usually be determined from optical data. The IP for the removal of an inner shell electron can be calculated from the experimental values of the energies of x-ray emission lines combined with the IP for the removal of the appropriate outer shell electron. For the 1*s*-hole IP's of Ne and Ar, the K absorption limits of gaseous Ne and Ar may be used. In Table VIII, the values of the experimental ionization potentials IP(exp) that are followed by a question mark were obtained from estimates or interpolations rather than from direct experimental data.

Except for the inert gases, Ar and Ne, the x-ray measurements used for Table VIII have not been made on free atomic systems, but rather on atoms in crystals. The wavelength and shape of the emission lines will, of course, be affected by the chemical structure of the solids. However, for the lines considered here, this chemical effect appears to be fairly small. The sources and interpretation of the experimental data used to obtain the values of IP(exp) given in Table VIII are discussed elsewhere.[15]

In certain cases, relativistic corrections are made to IP(exp) to obtain estimates of the nonrelativistic ionization potentials IP(nr). This was done in order to have a more meaningful comparison with the SCF values of the IP. The relativistic correction to the $1s$-hole IP is assumed to be equal to the relativistic correction to the IP of the two electron ions (IP for $1s^2$ to $1s^1$). The relativistic corrections to the IP's of the two electron ions are given by Pekeris[20] for $Z \leqslant 10$. Scherr and Silverman[21] have extrapolated Pekeris's results to $Z=20$. The relativistic correction to the $2p$-hole IP of an Ar-like ion is assumed to be equal to the relativistic correction to the IP of the ten electron ion (IP for $1s^2 2s^2 2p^6$ to $1s^2 2s^2 2p^5$). Scherr, Silverman, and Matsen[22] have calculated these corrections using screened nuclear charges to evaluate the relativistic part of the Dirac one-electron energy and the one-electron Lamb shift.

For the $2p$-hole IP's of the Ne-like ions and the $3p$-hole IP's of the Ar-like ions the only relativistic correction is that IP(exp) in Table VIII is given for the center of gravity of the ^2P term of the ion. Additional relativistic corrections for these cases should be rather small. No relativistic corrections are given for the $2s$-hole IP's of the Ne-like ions and the $2s$- and $3s$-hole IP's of the Ar-like ions. We have roughly estimated the relativistic correction to the IP for the removal of an electron from the outermost s shell using the method of Scherr, Silverman, and Matsen[22] with Slater's values of the screening constants. The correction is less than 0.005 Hartrees and will lower the value of IP(exp). The relativistic correction to the $2s$-hole IP of an Ar-like ion, estimated from the data of Scherr, Silverman, and Matsen,[22] is probably no more than 0.1 Hartrees and will also lower IP(exp).

A correction for the finite mass of the nucleus is included in the values of IP(exp) and IP(nr). The correction is made by multiplying the IP obtained from the experimental data for a finite mass nucleus by the factor $(1+m/M)$, where m is the electronic mass and M the nuclear mass.

It is possible to calculate the IP of a system in two ways from SCF wave functions. One way is to use the frozen-orbital approximation; i.e., to use the SCF orbitals of the parent system for both the parent and the ionized systems. In this approximation, the IP for the removal of an electron from the nl shell of a closed-shell system[2] is $-\epsilon_{nl}$ (Koopmans's theorem). The second way is to take the difference of the SCF total energies, ΔE_{SCF}, obtained from separate SCF calculations on the parent and the ion. In Table VIII we give the IP's calculated in these two ways, IP$(-\epsilon_{nl})$ and IP(ΔE_{SCF}), and their differences with the true values of the IP.

The true value of the IP, in the sense that it is used in this discussion, is the exact nonrelativistic value for a fixed nucleus. The error of an approximate value is the error with respect to this true value. The values of IP(exp) or IP(nr) given in Table VIII are taken to be good approximations to the true IP's. The choice of IP(exp) or IP(nr) depends, of course, on whether the electron has been removed from an inner or outer shell of the parent.

The data given in Table VIII show that when an electron is removed from the outermost shell ($2p$-shell of the Ne-like ions and $3p$-shell of the Ar-like ions), IP$(-\epsilon_{nl})$ is a better approximation than IP(ΔE_{SCF}) to the true IP. The explanation for this has been given by Mulliken.[23] When an electron is removed from any shell but the outermost shell, IP(ΔE_{SCF}) is a better approximation than IP$(-\epsilon_{nl})$ to the true IP. When an electron is removed from an inner shell ($1s$ shell of the Ne-like ions and $1s$, $2s$, or $2p$ shell of the Ar-like ions), the SCF orbitals of the ion are considerably different from the SCF orbitals of the parent (cf., $\langle r\rangle$ and $\langle r^2\rangle$ given in Tables VI and VII). Consequently, the error in using the orbitals of the closed-shell parent for these ions is quite large and the frozen orbital approximation is poor.

The SCF orbitals of the states which have a hole in the outermost s shell are not very different from the SCF orbitals of the states with a hole in the outermost p shell. For these s-hole states there is another reason why IP$(-\epsilon_{nl})$ is a poorer approximation than IP(ΔE_{SCF}). As discussed in Sec. IVA, these s-hole states are the lowest ^2S states of even parity of their ionic systems. When the ion is in the lowest state of a symmetry species, IP$(-\epsilon_{nl})$ must be greater than IP(ΔE_{SCF}).[24] However, IP(ΔE_{SCF}) for the removal of an outermost s electron is larger than the true IP. Since IP(ϵ_{nl}) must be still larger, it is a poorer approximation to the true IP. The surprising fact that IP(ΔE_{SCF}) is

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[20] C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).

[21] C. W. Scherr and J. N. Silverman, J. Chem. Phys. **37**, 1154 (1962).

[22] C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. **127**, 830 (1962). We are grateful to the authors for providing us, in a private communication, with the values of their screening constants.

[23] R. S. Mulliken, J. Chim. Phys. **46**, 497 (1949).

[24] There is no proof that the inequality IP$(-\epsilon_{nl}) >$ IP(ΔE_{SCF}) holds when an inner shell electron is removed since the resulting ion is not in the lowest state of a symmetry species. However, it may be seen from the results in Table VIII that this inequality does, in fact, hold for all the cases considered here.

larger than the true IP will be discussed in the next section.

The agreement of IP($\Delta E_{\rm SCF}$) with IP(nr) for the removal of an inner shell electron is remarkably good. The error of IP($\Delta E_{\rm SCF}$), for the cases where reliable experimental data and relativistic corrections are available, is always less than 0.2% and often no more than 0.1%. Thus, IP($\Delta E_{\rm SCF}$) often agrees with IP(nr) to *four* significant figures.

This good agreement is due, at least in part, to the fact that the importance of the one-electron contributions to the HF operator relative to the two-electron contributions (the kinetic energy and nuclear attraction terms relative to the Coulomb and exchange terms) is considerably greater for inner shell orbitals than for outer shell orbitals. The best results are obtained with the HF one-electron approximation when the two-electron terms are a small perturbation on the one-electron terms. The error of the HF treatment of the outer shell orbitals can be expected to be nearly the same whether an inner shell electron has been removed or not. Thus, IP($\Delta E_{\rm SCF}$) for the removal of an inner shell electron should give rather good agreement with the true IP.

No direct experimental data have been found for the $2s$-hole states of the Ar-like ions. Interpolations have been made by Tomboulian and Cady[25] for the term values of the $2s$-hole states of $\rm Cl^-$ and $\rm K^+$. [The interpolation method was based on rules for the $L_{\rm I}-L_{\rm II}$ ($2s$-hole, $^2S_{1/2}-2p$-hole, $^2P_{1/2}$) screening doublet splitting.] However, from the arguments above, IP($\Delta E_{\rm SCF}$) for the removal of a $2s$ electron from an Ar-like ion should be in good agreement with the true nonrelativistic IP. The relativistic correction for these IP's, estimated above, is probably no more than 0.1 Hartrees. Thus, even without relativistic corrections, IP($\Delta E_{\rm SCF}$) for these $2s$-hole states should agree with the *correct experimental* IP to within 1%. Because of the relativistic corrections, they should be smaller than the correct experimental values.

VI. ANOMALOUS BEHAVIOR OF THE CORRELATION ENERGY

The correlation energy $E_{\rm corr}$ is the error of the SCF total energy $E_{\rm SCF}$ and is defined by the relation

$$E_{\rm nr}=E_{\rm SCF}+E_{\rm corr}\,, \tag{10}$$

where $E_{\rm nr}$ is the exact nonrelativistic energy for a system with a fixed nucleus. The sign has been chosen so that $E_{\rm corr}$ is negative for all the systems considered here and is always negative for a state which is the lowest of a symmetry species. From the definition of the IP and Eq. (10), we have the relation

$$\text{IP(nr)}-\text{IP}(\Delta E_{\rm SCF})=E_{\rm corr}(\text{ion})-E_{\rm corr}(\text{parent})\,. \tag{11}$$

If the small relativistic corrections to IP(exp) for the removal of an electron from the outermost s or p shell are neglected, the error of IP($\Delta E_{\rm SCF}$) given in the last column of Table VIII is just the difference of the correlation energies of the parent and the ion.

Usually IP($\Delta E_{\rm SCF}$) is less than the true IP. The orbitals of the ion are not markedly different from those of the parent. The ion has one fewer electron than the parent, and it is reasonable to expect that $|E_{\rm corr}(\text{ion})| < |E_{\rm corr}(\text{parent})|$. This usual case occurs when an electron is removed from the outermost p shell of any of the closed-shell systems considered.

On the other hand, when an electron is removed from the outermost s shell IP($\Delta E_{\rm SCF}$) is *larger* than the true IP. If we neglect the small relativistic corrections, the magnitude of $E_{\rm corr}$ of $\rm Ne^+$($2s$-hole) is 0.84 eV *larger* than the magnitude of $E_{\rm corr}$ of Ne; $|E_{\rm corr}|$ of $\rm Ar^+$($3s$-hole) is 3.95 eV *larger* than $|E_{\rm corr}|$ of Ar. As noted in the previous section, the relativistic correction to IP(exp), in these cases, is less than 0.1 eV, and including it would make $|E_{\rm corr}|$ of the ion still larger than $|E_{\rm corr}|$ of the parent. When an electron is removed from the $2p$ or the $1s$ shell of one of the Ar-like ions, $|E_{\rm corr}|$ of the resulting ion is also larger than $|E_{\rm corr}|$ of the parent. The uncertainties of the experimental data and the relativistic corrections make this conclusion somewhat doubtful for the $2p$-hole states. For the $1s$-hole states, however, the increase of $|E_{\rm corr}|$ is larger than these uncertainties.

This anomalous behavior of the correlation energy is important in light of the recent work of Clementi[17] and, in particular, of Allen, Clementi, and Gladney[26] to obtain semiempirical rules for the calculation of $E_{\rm corr}$. Such rules, if they could be successfully applied, would be very useful since SCF wave functions may now be easily obtained for a large class of systems. However, the rules given by Allen, Clementi and Gladney fail to predict the anomalous correlation energies.

The analysis of Allen, Clementi, and Gladney is based on a decomposition of $E_{\rm corr}$ into pair correlation energies. For atoms, the pair correlation energy is denoted by $E_{\rm corr}(n,l,m_l,m_s;\,n',l',m_l',m_s')$, where n, l, m_l, m_s are the usual one-electron quantum numbers. They explicitly make three assumptions about this decomposition. (1) The total correlation energy is, to a very good approximation, the sum of the pair correlation energies,

$$E_{\rm corr}=\sum E_{\rm corr}(n,l,m_l,m_s;\,n',l',m_l',m_s')\,. \tag{12}$$

(2) The most important pair correlation energies are for electrons which differ only in their spin-quantum number and these correlation energies are independent of m_l; this is denoted by $E_{\rm corr}(n,l,m_l,\alpha;\,n,l,m_l,\beta) = E_{\rm corr}(n,l,\alpha;\,n,l,\beta)$. And (3), the pair-correlation energy, with minor qualifications, is a function only of the

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[25] D. H. Tomboulian and W. M. Cady, Phys. Rev. **59**, 422 (1941).

[26] L. C. Allen, E. Clementi, and H. M. Gladney, Rev. Mod. Phys. **35**, 465 (1963). In this paper the correlation energy is defined with the opposite sign of our correlation energy. The signs of their values, when quoted here, have been changed to conform to our sign convention.

quantum numbers of the pair of electrons and the nuclear charge Z; in particular it does not depend on the total electronic configuration of the system. The third assumption is a key one since Allen, Clementi, and Gladney obtained the pair correlation energies for an atom by subtracting the total correlation energies of various ions of the atom.

The first two assumptions are quite reasonable. The anomalous behavior of the correlation energy shows that the third assumption cannot be correct. When an electron is removed from the nl closed shell, it follows from the assumptions and from Eq. (11) that

$$-E_{\text{corr}}(n,l,\alpha;\, n,l,\beta) \cong E_{\text{corr}}(\text{ion}) - E_{\text{corr}}(\text{parent}) = \text{IP}(\text{nr}) - \text{IP}(\Delta E_{\text{SCF}}). \quad (13)$$

For Ne, Allen, Clementi, and Gladney find that $-E_{\text{corr}}(2p\alpha,2p\beta) \cong +1.7$ eV, $-E_{\text{corr}}(2s\alpha,2s\beta) \cong +3.2$ eV, and $-E_{\text{corr}}(1s\alpha,1s\beta) \cong +1.2$ eV. From the results given in Table VIII, we see that $E_{\text{corr}}(\text{Ne}^+;\, 2p \text{ hole}) - E_{\text{corr}}(\text{Ne}) = +1.75$ eV, $E_{\text{corr}}(\text{Ne}^+;\, 2s \text{ hole}) - E_{\text{corr}}(\text{Ne}) = -0.84$ eV and $E_{\text{corr}}(\text{Ne}^+;\, 1s \text{ hole}) - E_{\text{corr}}(\text{Ne}) = +0.65$ eV. When a $2p$ electron is removed Allen, Clementi, and Gladney correctly predict the change in the total correlation energy. This is hardly surprising since this change was part of the data used in their semiempirical analysis. However, when a $2s$ electron is removed they predict a *decrease* of $|E_{\text{corr}}|$ of ~ 3.2 eV; but, in fact, $|E_{\text{corr}}|$ *increases* by 0.84 eV. When a $1s$ electron is removed they predict that $|E_{\text{corr}}|$ decreases by ~ 1.2 eV, but the actual decrease is only half that. Allen, Clementi, and Gladney also give pair correlations for F and Na. Their predictions for the correlation energies of the nl-hole states of F^- and Na^+ are very similar to their predictions for Ne.

Kestner[27] has considered the anomalous correlation energy of the $2s$-hole state of Ne using the formalism of Sinonağlu. Kestner's explanation of the anomalous correlation energy is based on the increased importance of configuration interaction on the SCF wave function for $\text{Ne}^+(2s \text{ hole})$. He considers only configurations obtained by two electron replacements. The $1s^2 2s 2p^6$ configuration of $\text{Ne}^+(2s \text{ hole})$ can interact with configurations formed by placing only one electron into an orbital with principal quantum number $n > 2$; e.g., the configurations $1s^2 2s^2 2p^4 ns$, $1s^2 2s^2 2p^4 nd$ and $1s^2 2s 2p^5 np (2s\alpha 2p\beta \rightarrow 2s\beta np\alpha)$. Neutral Ne and $\text{Ne}^+(2p$ hole), however, can interact only with configurations formed by exciting *two* electrons into orbitals with $n > 2$. Thus, from energy considerations, the mixing of configurations will be larger for the $2s$-hole state than for the neutral atom or the $2p$-hole state. For the $2s$-hole state, where the effects of configuration interaction are more important, the SCF one configuration function gives a poorer approximation to the true wave function, and the magnitude of the correlation energy is larger. Similar arguments can be made about the $3s$-hole states of the Ar-like ions. The increase $|E_{\text{corr}}|$ for these states is more than four times larger than the increase of $|E_{\text{corr}}|$ for the $2s$-hole states of the Ne-like ions.

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[27] N. R. Kestner, (to be published).