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# Argonne National Laboratory

# SCF EXCITED STATES AND TRANSITION PROBABILITIES OF SOME NEON-LIKE AND ARGON-LIKE IONS

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by

Paul S. Bagus

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Scientific and Technical Information, National Bureau of Standards,
U. S. Department of Commerce, Springfield, Virginia

ANL-6959
Physics
(TID-4500, 37th Ed.)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60440

# SCF EXCITED STATES AND TRANSITION PROBABILITIES OF SOME NEON-LIKE and ARGON-LIKE IONS

by

Paul S. Bagus

Solid State Science Division

October 1964

This Work Provided the Basis for a
Thesis Submitted to the Department
of Physics, The University of Chicago
in Partial Fulfillment of the Require-
ments for the Degree of Doctor of Philosophy

Operated by The University of Chicago
under
Contract W-31-109-eng-38
with the
U. S. Atomic Energy Commission

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# ERRATUM

for

ANL-6959

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Page 44, second group, first line, last column, 0.1454 should read 0.1545; for $Ne^+(^2S)$ 1s-hole the $\langle r \rangle_{1s} = 0.1545$.

Alvin Glassner
Technical Publications Department

February 22, 1965

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# SCF EXCITED STATES AND TRANSITION PROBABILITIES OF SOME NEON-LIKE AND ARGON-LIKE IONS

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## ABSTRACT

Analytic self-consistent field (SCF) wave functions were computed for the ground states of the closed-shell atomic systems $F^-$, Ne, $Na^+$; and $Cl^-$, Ar, and $K^+$, and for those ground and excited states of the open-shell systems that 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 that 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 within 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 semi-empirical 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 argon. The effect of the nonzero off-diagonal Lagrangian multipliers is considered and found to be important for the inner-shell hole states. The SCF functions have been used to compute dipole transition probabilities for photon emission. The transition probabilities are computed in several different ways to examine the effects of various approximations. In particular, the results obtained using length, velocity, and acceleration operators are compared. The calculated radiation width for the K-state of argon is combined with an experimental value of the K-fluorescence yield to obtain a value of the total K-state width in agreement with experiment.

## I. INTRODUCTION

In this paper, analytical self-consistent field (SCF) functions are presented for the ground states of the closed-shell atomic systems $F^-$, Ne, $Na^+$, $Cl^-$, Ar, and $K^+$, and for those ground and excited states of the open-shell systems that are obtained by removing a single electron from any one of the occupied shells of these closed-shell systems. Specifically, we present SCF functions 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 SCF functions 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. They are also useful, for example, for calculating the effect of the electronic charge distribution on electron capture by the nucleus.(1)

Several properties of the wave functions have been calculated. Expectation values of $r$ and $r^2$ are given for the SCF orbitals and overlap integrals between total wave functions not orthogonal by symmetry. In the final section of this paper, dipole transition matrix elements between the wave functions are presented.

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. In its present form, the method will treat a system with any number of open shells, provided there is at most one open shell for each one-electron symmetry species.(2,3,4)

Extensive investigations have led to the development of reliable and accurate numerical techniques to implement the application of the analysis. These techniques have been incorporated into computer programs, written for the IBM 704, 7090, and 7094, for the calculation of atomic SCF wave functions.(4)

Many SCF calculations have been performed, using the Roothaan analysis, with the goal of obtaining accurate representations of the Hartree-Fock functions.(5-9) However, these functions have been for ground or low-lying excited states. The functions presented here are the first analytic SCF calculations for X-ray excited states of atomic systems. To our knowledge, the only numerical Hartree-Fock calculations for such states that correctly take exchange into account are those of Sureau and Berthier on aluminum.(10)

## II. THEORY

In the Roothaan expansion method, the SCF orbitals $\phi_{i\lambda\alpha}$, omitting spin, are given in terms of basis functions $\chi_{p,\lambda\alpha}$ by

$$\phi_{i\lambda\alpha} = \Sigma_p \, \chi_{p,\lambda\alpha} C_{i\lambda,p}. \tag{1}$$

Here $\lambda$ labels the symmetry species, and $\alpha$ the subspecies; for atoms, these are usually denoted by $\ell$ and m. The principal quantum number is represented by i, and p labels different basis functions of the same symmetry. The complete spin-orbital is given by

$$\psi_{i\lambda\alpha s} = \phi_{i\lambda\alpha}\,\eta_s, \tag{2a}$$

where

$$\eta_s = \alpha, \text{ or } \eta_s = \beta. \tag{2b}$$

The set of basis functions used in an expansion SCF wave function is referred to as the basis set of the function.

The notation used in Eqs. (1) and (2) is that adopted by Roothaan.(3,4) Since only atomic systems are considered in this paper, the standard notation for atomic orbitals, $n\ell m$, will be used, hereafter, in place of Roothaan's more general notation, $i\lambda\alpha$.

For atomic calculations, the basis functions are given by

$$\chi_{p,\ell m}(r,\theta,\phi) = R_{\ell p}(r)\,Y_{\ell m}(\theta,\phi), \tag{3}$$

where $Y_{\ell m}(\theta,\phi)$ are normalized spherical harmonics, and the radial functions $R_{\ell p}(r)$ are normalized nodeless Slater-type orbitals (STO's); namely,

$$R_{\ell p}(r;n_{\ell p},\zeta_{\ell p}) = [(2n_{\ell p})!]^{-\frac{1}{2}}(2\zeta_{\ell p})^{n_{\ell p}+\frac{1}{2}}\, r^{n_{\ell p}-1} e^{-\zeta_{\ell p} r}. \tag{4}$$

The integer $n_{\ell p}$ is called the principal quantum number of the basis function, and $\zeta_{\ell p}$ 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 that distinguishes that orbital from other orbitals of the same symmetry species and subspecies. The principal quantum number of an STO is merely a flexible parameter of a basis function. For example, in our calculations on argon, the 1s orbital is expanded in terms of 1s, 2s, and 3s STO's.

The choice of Slater-type orbitals for the radial functions $R_{\ell p}(r)$ is physically reasonable, and the computation of necessary integrals between STO's is simple (at least for atoms). Several expansion SCF calculations have been made on atomic systems with the goal of obtaining accurate functions using small basis sets of STO's. The results of these calculations agree quite well with Hartree-Fock (HF)* functions obtained by direct numerical integration.(9)

The many-electron wave function is constructed from one Slater determinant, or a linear combination of a few Slater determinants, of the occupied SCF orbitals. The combination is made so that the wave function is an eigenfunction of $\underset{\sim}{L}^2$, $\underset{\sim}{S}^2$, $L_z$, and $S_z$. (Methods for constructing eigenfunctions of angular momentum from Slater determinants are contained in Refs. 11 and 12.) The wave function is also an eigenfunction of the inversion operator and has a definite parity. The variational principle is applied to obtain equations for the coefficients $C_{n\ell,p}$[ $C_{i\lambda,p}$ in Eq. (1)]. These equations are then solved without further approximation. In particular, the off-diagonal Lagrangian multipliers, that couple equations for open- and closed-shell orbitals of the same symmetry are treated properly. (Procedures that treat the off-diagonal Lagrangian multipliers in an approximate way are contained in Refs. 13 and 14). It will be demonstrated in the discussion of the results that neglect of the off-diagonal Lagrangian multipliers significantly affects the SCF functions of certain excited states.

Equations (1), (2), and (3) place certain restrictions on the form of the SCF orbitals that should be stated explicitly. Equation (2) requires that the spin-orbital be factored into a product of a spatial function and a spin function. Equations (1) and (3) introduce the central field approximation by requiring that the orbital be factored into a product of a radial function and a spherical harmonic. A further consequence of Eqs. (1) and (3) is that all the electrons of a given shell have the same radial function. Thus, $\phi_{n\ell m}$ may be written as**

$$\phi_{n\ell m}(r,\theta,\phi) = F_{n\ell}(r) Y_{\ell m}(\theta,\phi), \tag{5}$$

where

$$F_{n\ell}(r) = \Sigma_p R_{\ell p}(r) C_{n\ell,p}. \tag{6}$$

---

*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.

**The use of F(r) to represent the radial portion of an orbital is an unfortunate deviation from the standard notation which is, of course, R(r). We do this to avoid confusion with the notation for the basis function $R_{\ell p}(r)$.

These orbitals are symmetry-adapted; i.e., they form bases for irreducible representations of the symmetry group of the (atomic) Hamiltonian. (For a discussion of the symmetry problem in the HF scheme, see Ref. 15.)

An additional requirement is that the occupied SCF orbitals form an orthonormal set,

$$\langle \phi_{n\ell m} | \phi_{n'\ell'm'} \rangle = \delta_{n\ell m, n'\ell'm'} . \tag{7a}$$

Because the orbitals are symmetry-adapted, this reduces to the requirement that

$$\int_0^\infty F^*_{n\ell}(r) F_{n'\ell}(r) r^2 \, dr = \delta_{n,n'} . \tag{7b}$$

In matrix notation, Eq. (7b) becomes

$$\underset{\sim}{c}^\dagger_{n\ell} \underset{\sim}{S}_\ell \underset{\sim}{c}_{n'\ell} = \delta_{n,n'} , \tag{7c}$$

where $\underset{\sim}{c}_{n\ell}$ is a vector that collects the coefficients $C_{n\ell,p}$, and $\underset{\sim}{S}_\ell$ is the overlap matrix of basis functions of symmetry species $\ell$,

$$S_{\ell pq} = \int_0^\infty R_{\ell p}(r) R_{\ell q}(r) r^2 \, dr . \tag{8}$$

In the numerical HF procedure, no assumption is made about the form of the radial function $F_{n\ell}(r)$. The variational principle is applied for arbitrary variations of the radial functions, subject to the constraint that they form an orthonormal set, and integro-differential equations for the $F_{n\ell}$'s are obtained.(2,3) (Reference 16 presents an excellent review of numerical Hartree-Fock procedures. Reference 17 discusses the applications of numerical techniques to high-speed digital computers.)

The solutions of the integro-differential equations satisfy the <u>cusp</u> <u>condition</u>,(18,19)

$$[(1/f_{n\ell})(df_{n\ell}/dr)]_{r=0} = -Z/(\ell+1), \tag{9a}$$

where

$$F_{n\ell}(r) = r^\ell f_{n\ell}(r) . \tag{9b}$$

The cusp condition may be used as a criterion for the accuracy of an expansion SCF orbital near the origin. Moreover, an orbital with a poor cusp value may be a poor representation of an exact HF orbital, not only in the region $r \to 0$, but also over the entire range of the function. The cusp condition is a necessary but not a sufficient condition that the orbital be a solution of the HF equations. A basis set can be chosen so that an expansion SCF orbital will satisfy the cusp conditions exactly;(8) however, the orbital may still be a poor approximation of the exact HF orbital.

The total Hamiltonian operator $\mathcal{H}$ for an atomic system may be written, in atomic units, as

$$\mathcal{H} = \mathcal{T} + \mathcal{V}, \qquad (10a)$$

where

$$\mathcal{T} = \Sigma_i\left(-\frac{1}{2}\Delta_i\right), \qquad (10b)$$

and

$$\mathcal{V} = -\Sigma_i(Z/r_i) + \Sigma_{i<j}(1/r_{ij}).$$

This Hamiltonian is valid for a system with nonrelativistic Coulomb interactions and an infinitely heavy nucleus.

If $\Psi$ is an exact eigenfunction of $\mathcal{H}$ for any bound state, then the virial theorem,

$$\langle\Psi|\mathcal{V}|\Psi\rangle / \langle\Psi|\mathcal{T}|\Psi\rangle = -2, \qquad (11)$$

is satisfied. If $\Psi$ is an approximate eigenfunction which contains a variable scale factor $k$ such that $\Psi(x_1, \ldots, x_n) = \Psi'(kx_1, \ldots, kx_n)$, and $k$ has been chosen to satisfy $(\partial/\partial k)(\langle\Psi'|\mathcal{H}|\Psi'\rangle / \langle\Psi'|\Psi'\rangle) = 0$, then this approximate $\Psi$ also satisfies Eq. (11).(20)

Exact HF functions satisfy the virial theorem since arbitrary variation of the radial part of the orbitals includes, implicitly, variation of a scale factor. Expansion SCF functions for an arbitrary basis set will not, in general, satisfy the virial theorem. If, however, variation of the exponents, as well as the linear coefficients, is performed, the virial theorem will be satisfied when all parameters have been optimized. Hence, for expansion SCF functions, the virial theorem is a necessary, but by no means sufficient, condition that an optimum basis set (in the sense of satisfying variational equations) has been used.

Let $\{\Psi(a)\}$ be a set of trial functions, where the index *a* distinguishes different members of the set from which we wish to choose an approximate wave function for some state of a system. The index *a* may represent a set of variable parameters, any one of which may be discrete or continuous. Let $\Psi(A)$ be chosen from the set $\{\Psi(a)\}$ as the solution of equations determined from application of the variational principle; i.e., $\Psi(A)$ satisfies

$$\delta_a[\langle\Psi(a)|\mathcal{H}|\Psi(a)\rangle/\langle\Psi(a)|\Psi(a)\rangle] = 0. \tag{12}$$

If $\Psi(A)$ is an approximate wave function for the ground state of the system or for the lowest excited state of a symmetry (*if the trial functions $\Psi(a)$ are symmetry-adapted*), then $\Psi(A)$ is the *best* function possible for the restricted form of the trial functions - *best* in the sense that the expectation value of the energy for $\Psi(A)$, $\langle\Psi(A)|\mathcal{H}|\Psi(A)\rangle = E(A)$, is more nearly equal to the true energy eigenvalue $E(t)$ than the expectation value of the energy for any of the other trial functions $\Psi(a)$. Moreover, $E(A) \geq E(t)$, and, if $E(A) = E(t)$, then $\Psi(A)$ is the true eigenfunction.(20,21)

This is not true for excited states that are not the lowest states of a symmetry *unless* the trial functions $\{\Psi(a)\}$ are constrained to be orthogonal to the exact eigenfunctions of all states of lower energy. The imposition of this constraint is, of course, not possible in general since the *exact* eigenfunctions of the lower states are not known. One procedure would be to require trial functions for excited states to be orthogonal to approximate wave functions for lower states. In the calculation of excited-state SCF functions, this is not done; no explicit requirement of orthogonality to lower SCF states is made.(8)

We rely on the physical model of the choice of the form of the SCF excited-state wave function to guarantee near-orthogonality to the SCF wave functions for lower-lying states. This physical model is, of course, the orbital or shell structure of the atom. Indeed, the only constraint that is imposed to obtain an excited-state, rather than a ground-state, wave function is the specification of the electronic configuration. For a 1s-hole state, for example, the HF operators are constructed on the assumption that the 1s 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 1s orbital is singly occupied is maintained throughout the process. The singly occupied 1s orbital is chosen at each iteration to be the eigenvector (of the appropriate HF operator) with the lowest orbital energy. This choice is easily justified by the fact that the orbital so chosen is the occupied orbital that is most similar to a hydrogenic 1s orbital.

The HF operators are functions of the electron density. The electron density of a complex atom does not change drastically in going from ground to excited states. Thus, the HF operators for ground and excited states are not drastically different, and SCF wave functions for excited states are very nearly orthogonal to SCF wave functions for lower states. The 3s-hole state of argon is the lowest $^2S$ state of $Ar^+$; the 1s-hole state, a very highly excited $^2S$ state, lies about 3000 eV above the 3s-hole state. Even for this extreme case, the overlap integral between the many-electron SCF wave functions for these two states, $\langle \Psi_{SCF}(1s\text{-hole}) | \Psi_{SCF}(3s\text{-hole}) \rangle$, is $5 \times 10^{-4}$. The requirement that the 1s-hole SCF wave function be orthogonal to the 3s-hole SCF wave function would produce only a very small change in the 1s-hole wave function. Further, since the 3s-hole SCF wave function is only an approximate eigenfunction, we do not know whether the constraint of orthogonality would improve or worsen the 1s-hole wave function. Overlap integrals between many-electron SCF wave functions for all those states, presented in this paper, that are not orthogonal by symmetry are given in Table XV. [M. Cohen and A. Daglarno(22) and D. Layzer(23) 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 $(1/Z)^2$.]

For a certain class of excited-state SCF wave functions, it is possible to state easily tested conditions that must be fulfilled in order that the SCF energy be an upper bound to the true energy of the state.(24)

# III: DETAILS OF THE CALCULATION OF THE SCF WAVE FUNCTIONS

To obtain analytic SCF orbitals that are good approximations to the exact orbitals, it is necessary to use a basis set that very nearly spans the true HF manifold. It is perhaps possible to do this by using large, more or less arbitrarily chosen, basis sets, but if this is done, several difficulties arise. Numerical processes that work well for basis sets of reasonable size become troublesome, and round-off error becomes important when large basis sets are used. Long expansions of atomic functions are poor starting points for molecular and solid-state calculations, while short expansions have proved to be excellent starting points for molecular SCF calculations.(25) By using large basis sets, one loses much of the advantage of simplicity that the analytic representation of SCF functions has over numerical tables of orbitals. For large atomic systems, the finite size of the computer becomes an important limiting factor on the size of the basis set.

For these reasons, we have used basis sets of limited size, making a careful choice of the exponents and principal quantum numbers of the STO's in order to minimize the total SCF energy. Particular emphasis is placed on varying the exponents to find optimum values. This variation is performed automatically by the computer program.(4) Our method of exponent variation is to perform several complete SCF calculations for different values of the exponents and to interpolate between these values.

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. The particular stationary value that we obtain is a minimum. Explicit variational equations for the exponents as well as the linear coefficients $C_{n\ell,p}$ have been given by Dehn.(26) The equations for the exponents appear to be difficult to solve. One important problem is that the basis functions used to represent an SCF orbital (to a given accuracy) are by no means uniquely determined.(27,28) Our brute-force variation of the exponents has proved to be a quite satisfactory procedure.

When basis sets of limited size are used, it is important 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 can give only a crude approximation to the exact HF wave function, but for a small set it is easy to find the optimum values of the principle quantum numbers and exponents. This gives a first or base reference point for more accurate calculations on the state. 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. In this way, it is possible to gauge the "need" for the new basis function, and to make an educated guess about the "need" for an additional basis function. The intermediate sets, formed in this build-up process, are often useful in themselves.

Because of the many SCF calculations involved in the optimization of the basis set, the experience gained in the calculation of one state must be applied to the calculation of similar states of the same or neighboring atoms. Linear extrapolations and interpolations of the exponents for states already computed provide good approximations to the optimized exponents of a nearby state. This is particularly true for smaller basis sets, since for these sets the optimum values of the exponents are well-defined. For larger basis sets, where several different sets of values of the exponents will give functions with the same total energy, the interpolated and extrapolated values provide a good starting point for exponent variations that lead to the optimized values.

Thus the calculation of the functions of a series of states must be done systematically, and the function for each state must not be computed as a separate problem. This systematic procedure will also uncover errors in optimization of basis sets. 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. While 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.

It will be useful, for the following discussion, to introduce the notion of a loop of an orbital. A hydrogenic radial function with quantum numbers $n\ell$ has $n - \ell - 1$ nodes and $n - \ell$ loops between these nodes and the points $r = 0$ and $r = \infty$. Similarly, the HF radial function $F_n$ (r) generally has $n - \ell - 1$ nodes and $n - \ell$ loops. The contributions to the HF operator of exchange terms and off-diagonal Lagrangian multipliers will introduce, in exceptional cases, extra nodes and loops near the tail of the orbital;* but the function is very small in these loops, and for this discussion they may be ignored. For HF orbitals of a particular state of a system, the 1s orbital and the inner loops of the 2s and 3s orbitals, in a rough sense, occupy the same region of space. Similarly, the outer loop of the 2s orbital and the middle loop of the 3s orbital occupy the same region of space. Thus, for a given state of a system, the $n^{th}$ loops of HF orbitals of the same symmetry roughly define a distinct range of values of $r$. The range is rather well-defined, except for an outer loop. The outer loop of an orbital always has a long "tail" going slowly to zero. This division of $r$ into distinct ranges permits us to consider groups of basis functions, where each group is chosen to fit a particular loop.

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*See Ref. 29 and the discussion in Section IV-E of this paper.

The computer program used for the SCF calculations has facilities for the coupled variation of the exponents of one, two, or three basis functions. The choice of the exponents to be varied, if any, is part of the input data to a run.

When the exponent of one basis function is varied, the program performs complete SCF calculations for different values of the exponent being varied while all the other exponents are held fixed. An energy minimum is found and bracketed by calculations for five values of the exponent at intervals of $\frac{1}{2}\Delta\zeta$. The optimum value of the exponent is determined by interpolation; a quartic is fit to these five points and its minimum is obtained. The exponent variation increment, $\Delta\zeta$, is a flexible input parameter.

Care must be taken in the choice of $\Delta\zeta$ so that the interpolation may be accurate. If $\Delta\zeta$ is chosen too small, the differences of the calculated SCF energies will be small and the interpolation will be in error because of the round-off errors in the SCF energies. This is not too serious since the optimum value of the exponent is indeterminate because of this round-off error in the SCF energies; however, fairly large amounts of computer time may be wasted by trying to bracket the energy minimum too closely. Moreover, if the energy differences are small enough, a true energy minimum may be missed because the round-off in the SCF energies causes an apparent, but false, minimum. Since, for calculations of the size presented here, the round-off error in the SCF energy appears to be a few units in the eighth significant figure, we tried to choose $\Delta\zeta$ so that the SCF energy changed by at least a few units in the seventh significant figure between adjacent SCF calculations.

If $\Delta\zeta$ is chosen too large, the interpolation will be in error because the points (in exponent space) at which SCF calculations are made are too far apart to be fit meaningfully by a quartic. The usual symptom of this is large changes in the SCF vector coefficients $C_{n\ell,p}$ between adjacent points. These changes indicate that the basis function is being "used" in the SCF orbitals in qualitatively different ways for different values of the exponent. The best, simple way to test whether $\Delta\zeta$ has been chosen too large is to compare the interpolated value of the total energy with the energy obtained from an SCF calculation using the interpolated value of the exponent. This SCF calculation is automatically performed by the program.

The quartic interpolation scheme is sufficiently accurate so that, for a properly chosen $\Delta\zeta$, the predicted and computed values of the energy will agree within round-off error. The range of acceptable values of $\Delta\zeta$ is, in fact, quite large, and only in exceptional cases must $\Delta\zeta$ be given to more than one or one and one-half significant figures.

The procedures for the coupled variation of two and three exponents are an extension of those described above for the variation of a single exponent. However, while a one-dimensional variation requires at least five SCF calculations, a two-dimensional variation requires at least 25 SCF calculations, and a three-dimensional variation requires at least 125.

Multidimensional variations should couple the exponents of basis functions used to represent a loop of the orbitals. They should not couple the exponents of basis functions used to represent different loops. A multidimensional variation will usually give better values for the exponents than a series of one-dimensional variations since a larger region of exponent space is examined in a multidimensional variation. However, a multidimensional variation may use more computer time than a series of one-dimensional variations. The exponent variation procedures are described in detail elsewhere.(4)

The principal quantum numbers of the STO's of a basis set can be chosen in a special way so that the cusp condition of Eq. (9) is automatically satisfied for all the SCF orbitals.(8) We call a basis set of STO's whose principal quantum numbers have been chosen in this special way a fixed-cusp set. Extensive experience, especially for first-row atoms,(9) but also for some second-row atoms,(30) has shown that if fixed-cusp sets are not used it is possible to obtain <u>accurate</u> SCF orbitals with adequate cusp values using smaller basis sets. Often the best energies obtained using these free-cusp sets were lower than the best energies obtained using the larger fixed-cusp sets. For this reason, we choose to use free-cusp sets.

Whereas 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 that 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 the fluorine, neon, and sodium ions, we used 2p STO's to represent the 2p orbital; and for the states of the chlorine, argon, and potassium ions, we used 3s STO's to represent the outer loop of the 3s orbital.

This was by no means a hard and fast rule; we did limited experimentation with other values. The need for experimentation was usually indicated by one of the following three factors:

1. The failure of the automatic exponent variation procedures of our computer programs to operate efficiently. The program would vary the exponents so as to cause the basis set to become nearly redundant; that is, the basis functions at some stage of the exponent variation process would form a nearly linearly dependent set.*

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* A precise measure of the redundancy of a basis set is the value of the determinant of the overlap matrix $S$ of the basis functions. As the determinant of $S$ goes to zero, the basis set goes to complete redundancy (exact linear dependence).

2. The failure of a subset of the full basis set to adequately represent a loop. This is indicated when a basis function that is important in a region of space outside the loop does not have a small coefficient when it contributes to the representation of the loop. Consider the 1s orbital of neutral argon, for example. For the accurate SCF function (see Table III), the principal quantum numbers of the basis functions that represent the inner s-loop are 1, 2, and 3. The coefficients of these functions for the 1s orbital are large, and the 1s coefficients $C_{1s,p}$ of the remainder of the s basis functions are of the order of $1 \times 10^{-4}$. We tried to obtain an SCF function of the same accuracy using two 1s and one 3s basis functions to represent the inner s-loop. In this case, the 1s coefficients of the remainder of the s basis functions were as large as $2 \times 10^{-2}$.

3. The desirability of keeping the basis set as nearly linearly independent as possible. For the states of the chlorine, argon, and potassium ions, we believe that we have a less redundant basis set if we use three 2p and one 4p basis functions to represent the inner p-loop, than if we were to use four 2p basis functions. This consideration is important only when we come to the final, largest basis sets used to obtain the most accurate SCF wave functions.

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

Because of the limitations of the computer, the total energy is only computed to eight significant figures. The contribution of the outer shells to $E_{SCF}$ is masked by the large contributions of the core. A rough measure of the contribution of an electron in the $n\ell$-shell to $E_{SCF}$ is the orbital energy $\epsilon_{n\ell}$. For neutral argon, we have the values $E_{SCF} = -526.817$, $\epsilon_{1s} = -119.610$, and $\epsilon_{3s} = -1.277$; the unit of energy is the Hartree (1 Hartree = 27.2098 eV). Thus, when exponent variations are performed on the inner s-loop basis functions, there are effectively two more significant figures in $E_{SCF}$ to examine than when exponent variations are performed on the outer s-loop basis functions. To produce equal changes in $E_{SCF}$, larger changes must be made in the exponents (and therefore in the orbitals) of the basis functions used to represent outer loops than in the exponents of the basis functions used to represent inner loops.

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 total SCF energy when choosing the basis functions used to represent the outer loops of the 3s and 3p orbitals of the states of the chlorine, argon, and potassium 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 are 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, so that the tails of the orbitals would be fit properly. The tails of the orbitals make the smallest contribution to the total energy. Thus, 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 calculations reported here were performed with computer programs written for the IBM 704 and 7090/4 by Professor C. C. J. Roothaan and the author, 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 SCF CALCULATIONS

## A. The SCF Wave Functions

Tables I-IV present the most accurate SCF function computed for each state. Tables V-VIII present a simpler, less accurate, but quite useful SCF function for each state. The simple basis sets were obtained with relatively little computational effort. They are a good starting point for extending these calculations to other states of interest (for example, to states formed in X-ray absorption). In addition, the simple basis set functions are sufficiently accurate for many purposes. Expectation values of r and $r^2$, dipole-transition matrix elements, and overlap of SCF wave functions were computed with the simple set SCF functions as well as the accurate set SCF functions. The values obtained usually agree quite well. Some comparisons that indicate the extent of the agreement will be given later.

The results in Tables I-VIII include the total energy for the non-relativistic, electrostatic, fixed-nucleus Hamiltonian of Eq. (10) 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 are given in parentheses 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 $\epsilon_{n\ell}$, the cusp [defined in Eq. (9)], and the vector coefficients $C_{n\ell,p}$ are given. The numbering of the vector coefficients corresponds to the numbering of the basis functions. All energies are given in Hartrees. The results reported in Tables I-VIII are from calculations performed on an IBM 7094.

The total wave functions for the states given in Tables I-VIII 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 1s-hole states of $F^-$, Ne, and $Na^+$, and the 1s-, 2s-, and 2p-hole states of $Cl^-$, Ar, and $K^+$ are not the lowest states of their symmetry species; these states are marked with asterisks in Tables I-VIII.

The 2s-hole states of Ne and $Na^+$, and the 3s-hole states of Ar and $K^+$ are the first excited states of $Ne^+$, $Na^{++}$, $Ar^+$, and $K^{++}$, respectively. They are the lowest $^2S$ states.

The 2s-hole state of $F^-$ is a highly excited state of fluorine; it is, in fact, past the ionization limit. However, Moore(31) does not give any other $^2S$ state of even parity in the spectrum of fluorine. The 3s-hole state of $Cl^-$ is not observed, but no $^2S$ states of even parity are observed in the spectrum of chlorine.(31) Thus these states may be the lowest states of their symmetry species.

TABLE I. 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 | $F(^2S)$ 1s-hole | $Ne(^1S)$ | $Ne^+(^2P)$ 2p-hole | $Ne^+(^2S)$ 2s-hole | $Ne^+(^2S)$* 1s-hole | $Na^+(^1S)$ | $Na^{++}(^2P)$ 2p-hole | $Na^{++}(^2S)$ 2s-hole | $Na^{++}(^2S)$* 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 | -2.00000 |
| $\zeta_1(1s)$ | 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 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| $\epsilon_{1s}$ | -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 | .... | .... | .... | .... | .... | .... | ..... | .... | .... | .... | .... |
| $\epsilon_{2s}$ | -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 | .... | .... | .... | ..... | .... | .... | .... | .... | .... | .... | .... |
| $\epsilon_{2p}$ | -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 | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... | .... |

*States which are not the lowest of a symmetry species.

TABLE II. SCF Orbitals and Energies for Cl⁻ and $n\ell$-hole States of Cl⁻, Accurate Basis Sets

| | $Cl^-(^1S)$ | $Cl(^2P)$ 3p-hole | $Cl(^2S)$ 3s-hole | $Cl(^2P)^*$ 2p-hole | $Cl(^2S)^*$ 2s-hole | $Cl(^2S)^*$ 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 |
| $\epsilon_{1s}$ | -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 |
| $\epsilon_{2s}$ | -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 | 0.00443 | 0.00693 |
| $c_{2s,7}$ | -0.00023 | -0.00015 | 0.00006 | 0.00042 | 0.00979 | -0.00024 |
| $\epsilon_{3s}$ | -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 |
| $\epsilon_{2p}$ | -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 |
| $\epsilon_{3p}$ | -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 | -0.07359 |
| $c_{3p,5}$ | 0.59454 | 0.60295 | 0.62287 | 0.63710 | 0.63463 | 0.63024 |
| $c_{3p,6}$ | 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 |

*States which are not the lowest of a symmetry species.

TABLE III. SCF Orbitals and Energies for Argon and $n\ell$-hole States of Argon, Accurate Basis Sets

| | Ar($^1$S) | Ar$^+$($^2$P) 3p-hole | Ar$^+$($^2$S) 3s-hole | Ar$^+$($^2$P)* 2p-hole | Ar$^+$($^2$S)* 2s-hole | Ar$^+$($^2$S)* 1s-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 | 2.350 | 2.305 |
| $\zeta_7$(3p) | 1.370 | 1.550 | 1.550 | 1.620 | 1.620 | 1.650 |
| $\epsilon_{1s}$ | -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 | 0.83065 |
| $c_{1s,2}$ | 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 |
| $\epsilon_{2s}$ | -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 |
| $\epsilon_{3s}$ | -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 |
| $\epsilon_{2p}$ | -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 |
| $\epsilon_{3p}$ | -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 |

*States which are not the lowest of a symmetry species.

TABLE IV. SCF Orbitals and Energies for $K^+$ and $n\ell$-hole States of $K^+$, Accurate Basis Sets

|  | $K^+(^1S)$ | $K^{++}(^2P)$ 3p-hole | $K^{++}(^2S)$ 3s-hole | $K^{++}(^2P)$* 2p-hole | $K^{++}(^2S)$* 2s-hole | $K^{++}(^2S)$* 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 |
| $\epsilon_{1s}$ | -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 |
| $\epsilon_{2s}$ | -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 | 0.14000 | 0.14292 | 0.15844 | 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 |
| $\epsilon_{3s}$ | -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 |
| $\epsilon_{2p}$ | -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 |
| $\epsilon_{3p}$ | -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 |

*States which are not the lowest of a symmetry species.

TABLE V. SCF Orbitals and Energies for $F^-$, Ne, and $Na^+$ and $n\ell$-hole States of $F^-$, Ne, and $Na^+$, Simple Basis Sets

| | $F^-(^1S)$ | $F(^2P)$<br>2p-hole | $F(^2S)$<br>2s-hole | $F(^2S)^*$<br>1s-hole | $Ne(^1S)$ | $Ne^+(^2P)$<br>2p-hole | $Ne^+(^2S)$<br>2s-hole | $Ne^+(^2S)^*$<br>1s-hole | $Na^+(^1S)$ | $Na^{++}(^2P)$<br>2p-hole | $Na^{++}(^2S)$<br>2s-hole | $Na^{++}(^2S)^*$<br>1s-hole |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| E | -99.45785 | -99.40893 | -98.53085 | -74.52382 | -128.5465 | -127.8176 | -126.7346 | -96.62555 | -161.6766 | -159.9972 | -158.7087 | -121.7423 |
| V/T | -2.000002 | -2.000004 | -1.999999 | -1.999993 | -2.000008 | -2.000018 | -2.000004 | -1.999990 | -2.000002 | -2.000013 | -1.999996 | -1.999995 |
| $\zeta_1(1s)$ | 13.220 | 13.198 | 12.810 | 12.758 | 14.319 | 13.623 | 13.859 | 12.382 | 15.314 | 14.403 | 14.659 | 12.211 |
| $\zeta_2(1s)$ | 8.282 | 8.278 | 8.230 | 8.842 | 9.224 | 9.144 | 9.162 | 9.729 | 10.157 | 10.033 | 10.058 | 10.420 |
| $\zeta_3(3s)$ | 4.952 | 4.982 | 4.962 | 5.225 | 5.619 | 5.627 | 5.576 | 5.926 | 6.254 | 6.233 | 6.172 | 6.676 |
| $\zeta_4(2s)$ | 2.094 | 2.246 | 2.293 | 2.369 | 2.518 | 2.700 | 2.734 | 2.840 | 2.966 | 3.161 | 3.189 | 3.328 |
| $\zeta_1(2p)$ | 5.219 | 6.165 | 6.112 | 5.695 | 6.620 | 7.588 | 7.405 | 6.665 | 8.000 | 9.058 | 8.759 | 7.515 |
| $\zeta_2(2p)$ | 2.599 | 3.176 | 3.144 | 3.208 | 3.484 | 3.991 | 3.926 | 3.955 | 4.316 | 4.794 | 4.715 | 4.624 |
| $\zeta_3(2p)$ | 1.154 | 1.612 | 1.582 | 1.724 | 1.766 | 2.164 | 2.122 | 2.276 | 2.325 | 2.698 | 2.651 | 2.799 |
| $\epsilon_{1s}$ | -25.82687 | -26.38217 | -26.42007 | -29.53598 | -32.77162 | -33.61208 | -33.61587 | -37.16972 | -40.75946 | -41.86265 | -41.83046 | -45.82011 |
| Cusp | -9.01242 | -9.01302 | -9.00866 | -9.02632 | -10.01011 | -9.99551 | -10.00523 | -10.02222 | -11.00542 | -10.98715 | -10.99733 | -11.01931 |
| $C_{1s,1}$ | 0.07956 | 0.08056 | 0.09582 | 0.02797 | 0.08650 | 0.11485 | 0.10566 | 0.08021 | 0.09647 | 0.14038 | 0.12778 | 0.28471 |
| $C_{1s,2}$ | 0.92438 | 0.92348 | 0.90835 | 0.96451 | 0.91716 | 0.88966 | 0.89831 | 0.91277 | 0.90707 | 0.86426 | 0.87630 | 0.70895 |
| $C_{1s,3}$ | 0.00594 | 0.00580 | 0.00607 | 0.01658 | 0.00595 | 0.00408 | 0.00588 | 0.01441 | 0.00573 | 0.00315 | 0.00501 | 0.01183 |
| $C_{1s,4}$ | -0.00032 | -0.00044 | 0.00019 | 0.01639 | -0.00029 | 0.00019 | 0.00015 | 0.01595 | -0.00031 | 0.00045 | 0.00034 | 0.01596 |
| $\epsilon_{2s}$ | -1.07236 | -1.57205 | -1.70549 | -1.74516 | -1.92975 | -2.61894 | -2.75289 | -2.85336 | -3.07347 | -3.93044 | -4.06561 | -4.22285 |
| Cusp | -9.07531 | -8.99798 | -9.00934 | -8.94043 | -10.01357 | -9.95997 | -9.96417 | -9.95186 | -10.96458 | -10.93106 | -10.93216 | -10.97567 |
| $C_{2s,1}$ | -0.00824 | -0.00411 | -0.00583 | 0.01728 | -0.00431 | -0.00220 | -0.00127 | 0.03807 | -0.00001 | 0.00192 | 0.00298 | 0.05695 |
| $C_{2s,2}$ | -0.22858 | -0.24286 | -0.24667 | -0.29148 | -0.24635 | -0.26184 | -0.26625 | -0.32867 | -0.26474 | -0.28137 | -0.28516 | -0.36558 |
| $C_{2s,3}$ | 0.33891 | 0.29770 | 0.29412 | 0.30914 | 0.29901 | 0.26352 | 0.26319 | 0.26448 | 0.26942 | 0.23998 | 0.23945 | 0.22166 |
| $C_{2s,4}$ | 0.73161 | 0.76464 | 0.76645 | 0.75408 | 0.76514 | 0.79565 | 0.79427 | 0.79696 | 0.79097 | 0.81852 | 0.81770 | 0.84308 |
| $\epsilon_{2p}$ | -0.17886 | -0.72953 | -0.70231 | -0.87121 | -0.84974 | -1.60644 | -1.55239 | -1.81586 | -1.79697 | -2.74424 | -2.66290 | -3.01944 |
| Cusp | -4.02916 | -4.19515 | -4.20656 | -4.32426 | -4.67506 | -4.78652 | -4.78530 | -4.86452 | -5.26728 | -5.35367 | -5.34729 | -5.38621 |
| $C_{2p,1}$ | 0.14234 | 0.07255 | 0.07692 | 0.13992 | 0.08944 | 0.04870 | 0.05544 | 0.11167 | 0.06123 | 0.03406 | 0.04050 | 0.10024 |
| $C_{2p,2}$ | 0.56283 | 0.48890 | 0.49372 | 0.49635 | 0.50024 | 0.43454 | 0.44020 | 0.44736 | 0.45069 | 0.39047 | 0.39581 | 0.40934 |
| $C_{2p,3}$ | 0.43109 | 0.53155 | 0.52539 | 0.45645 | 0.50722 | 0.58891 | 0.57919 | 0.51414 | 0.56481 | 0.63486 | 0.62536 | 0.55122 |

*States which are not the lowest of a symmetry species.

TABLE VI. SCF Orbitals and Energies for Cl⁻ and $n\ell$-hole States of Cl⁻, Simple Basis Sets

| | Cl⁻($^1S$) | Cl($^2P$)<br>3p-hole | Cl($^2S$)<br>3s-hole | Cl($^2P$)*<br>2p-hole | Cl($^2S$)*<br>2s-hole | Cl($^2S$)*<br>1s-hole |
|---|---|---|---|---|---|---|
| E | -459.5736 | -459.4801 | -458.9148 | -452.3332 | -449.7638 | -356.2814 |
| V/T | -2.000000 | -1.999993 | -2.000007 | -1.999991 | -2.000000 | -1.999988 |
| $\zeta_1$(1s) | 18.575 | 18.674 | 18.629 | 18.474 | 18.095 | 17.749 |
| $\zeta_2$(2s) | 16.329 | 16.439 | 16.385 | 16.245 | 15.621 | 16.424 |
| $\zeta_3$(3s) | 10.217 | 10.190 | 10.219 | 10.021 | 10.386 | 10.381 |
| $\zeta_4$(2s) | 5.798 | 5.785 | 5.795 | 5.895 | 6.062 | 6.082 |
| $\zeta_5$(3s) | 2.823 | 2.904 | 2.878 | 3.140 | 3.030 | 3.167 |
| $\zeta_6$(3s) | 1.651 | 1.826 | 1.842 | 1.970 | 1.923 | 1.982 |
| $\zeta_1$(2p) | 10.203 | 10.268 | 10.275 | 10.586 | 10.594 | 10.460 |
| $\zeta_2$(2p) | 5.585 | 5.608 | 5.610 | 5.884 | 5.841 | 6.002 |
| $\zeta_3$(3p) | 2.497 | 2.612 | 2.617 | 2.787 | 2.798 | 2.881 |
| $\zeta_4$(3p) | 1.224 | 1.465 | 1.459 | 1.570 | 1.576 | 1.607 |
| $\epsilon_{1s}$ | -104.50086 | -104.88211 | -104.95369 | -106.26874 | -106.03937 | -112.50146 |
| Cusp | -16.96350 | -16.96634 | -16.96577 | -16.95669 | -16.95214 | -17.01951 |
| $C_{1s,1}$ | 0.85189 | 0.84517 | 0.84820 | 0.85920 | 0.88567 | 0.92623 |
| $C_{1s,2}$ | 0.17649 | 0.18395 | 0.18062 | 0.16830 | 0.13937 | 0.07920 |
| $C_{1s,3}$ | -0.00074 | -0.00011 | -0.00046 | -0.00234 | -0.00594 | 0.01076 |
| $C_{1s,4}$ | 0.00245 | 0.00217 | 0.00237 | 0.00337 | 0.00593 | 0.01019 |
| $C_{1s,5}$ | -0.00052 | -0.00054 | -0.00061 | -0.00082 | -0.00112 | -0.00151 |
| $C_{1s,6}$ | 0.00021 | 0.00024 | 0.00027 | 0.00034 | 0.00051 | -0.00221 |
| $\epsilon_{2s}$ | -10.22595 | -10.60672 | -10.66476 | -11.32012 | -11.47338 | -11.83108 |
| Cusp | -16.99022 | -16.97968 | -16.98170 | -16.99964 | -17.00832 | -16.98680 |
| $C_{2s,1}$ | -0.23882 | -0.23691 | -0.23743 | -0.24544 | -0.25239 | -0.27771 |
| $C_{2s,2}$ | 0.11908 | -0.11959 | -0.11987 | -0.11900 | -0.13056 | -0.10274 |
| $C_{2s,3}$ | 0.14005 | 0.14504 | 0.13795 | 0.17025 | 0.09289 | 0.15200 |
| $C_{2s,4}$ | 0.93670 | 0.93089 | 0.93755 | 0.91033 | 0.98751 | 0.93066 |
| $C_{2s,5}$ | 0.00654 | 0.00546 | 0.00782 | 0.00241 | 0.02434 | 0.00530 |
| $C_{2s,6}$ | -0.00035 | 0.00010 | -0.00001 | 0.00185 | 0.01004 | 0.00059 |
| $\epsilon_{3s}$ | -0.73031 | -1.07236 | -1.17505 | -1.22270 | -1.20752 | -1.23049 |
| Cusp | -16.76015 | -16.72967 | -16.74820 | -16.62437 | -16.83732 | -16.69588 |
| $C_{3s,1}$ | 0.07001 | 0.07132 | 0.07321 | 0.07805 | 0.08474 | 0.08627 |
| $C_{3s,2}$ | 0.04802 | 0.05010 | 0.05117 | 0.05897 | 0.06448 | 0.05180 |
| $C_{3s,3}$ | 0.01033 | 0.01482 | 0.01573 | 0.03488 | 0.04751 | 0.03199 |
| $C_{3s,4}$ | -0.42149 | -0.44112 | -0.45062 | -0.50811 | -0.53027 | -0.49176 |
| $C_{3s,5}$ | 0.70660 | 0.65189 | 0.68576 | 0.64632 | 0.67235 | 0.64391 |
| $C_{3s,6}$ | 0.43162 | 0.48073 | 0.44446 | 0.50908 | 0.46670 | 0.50380 |
| $\epsilon_{2p}$ | -7.69225 | -8.07136 | -8.14535 | -9.00648 | -8.78900 | -9.55916 |
| Cusp | -8.06915 | -8.08454 | -8.08774 | -8.12583 | -8.14560 | -8.32563 |
| $C_{2p,1}$ | 0.21126 | 0.20561 | 0.20543 | 0.17599 | 0.17940 | 0.21911 |
| $C_{2p,2}$ | 0.81783 | 0.82121 | 0.82229 | 0.83577 | 0.84306 | 0.80592 |
| $C_{2p,3}$ | 0.01585 | 0.02020 | 0.01796 | 0.03725 | 0.01956 | 0.01500 |
| $C_{2p,4}$ | -0.00394 | -0.00457 | -0.00509 | 0.01137 | -0.00519 | -0.00369 |
| $\epsilon_{3p}$ | -0.14772 | -0.50603 | -0.50013 | -0.58933 | -0.58439 | -0.59575 |
| Cusp | -8.14508 | -8.12119 | -8.12953 | -8.12036 | -8.13553 | -8.37302 |
| $C_{3p,1}$ | -0.05028 | -0.05192 | -0.05186 | -0.05079 | -0.04652 | -0.05670 |
| $C_{3p,2}$ | -0.21340 | -0.23694 | -0.23666 | -0.28976 | -0.26765 | -0.24645 |
| $C_{3p,3}$ | 0.61008 | 0.56419 | 0.57193 | 0.59434 | 0.59193 | 0.58595 |
| $C_{3p,4}$ | 0.52453 | 0.54343 | 0.53765 | 0.51794 | 0.52288 | 0.52859 |

*States which are not the lowest of a symmetry species.

TABLE VII. SCF Orbitals and Energies for Argon and $n\ell$-hole States of Argon, Simple Basis Sets

| | Ar($^1$S) | Ar$^+$($^2$P) 3p-hole | Ar$^+$($^2$S) 3s-hole | Ar$^+$($^2$P)* 2p-hole | Ar$^+$($^2$S)* 2s-hole | Ar$^+$($^2$S)* 1s-hole |
|---|---|---|---|---|---|---|
| E | -526.8155 | -526.2729 | -525.5961 | -517.6676 | -514.8779 | -409.3884 |
| V/T | -2.000001 | -2.000001 | -1.999997 | -2.000000 | -2.000002 | -2.000015 |
| $\zeta_1$(1s) | 19.419 | 19.412 | 19.454 | 19.138 | 19.045 | 18.566 |
| $\zeta_2$(2s) | 17.034 | 17.024 | 17.075 | 16.639 | 16.371 | 16.958 |
| $\zeta_3$(3s) | 10.943 | 10.941 | 10.896 | 10.896 | 11.085 | 11.082 |
| $\zeta_4$(2s) | 6.275 | 6.279 | 6.277 | 6.436 | 6.537 | 6.562 |
| $\zeta_5$(3s) | 3.187 | 3.259 | 3.232 | 3.474 | 3.314 | 3.532 |
| $\zeta_6$(3s) | 2.005 | 2.185 | 2.201 | 2.311 | 2.230 | 2.340 |
| $\zeta_1$(2p) | 11.027 | 11.073 | 11.095 | 11.402 | 11.417 | 11.208 |
| $\zeta_2$(2p) | 6.095 | 6.113 | 6.120 | 6.388 | 6.345 | 6.498 |
| $\zeta_3$(3p) | 2.886 | 2.956 | 2.972 | 3.127 | 3.142 | 3.234 |
| $\zeta_4$(3p) | 1.609 | 1.814 | 1.812 | 1.919 | 1.928 | 1.963 |
| $\epsilon_{1s}$ | -118.60817 | -119.13197 | -119.19307 | -120.65641 | -120.39431 | -127.27928 |
| Cusp | -17.95816 | -17.95800 | -17.95995 | -17.94695 | -17.95166 | -18.01716 |
| $C_{1s,1}$ | 0.86927 | 0.86975 | 0.86693 | 0.88877 | 0.89477 | 0.94351 |
| $C_{1s,2}$ | 0.15689 | 0.15636 | 0.15949 | 0.13538 | 0.12918 | 0.05966 |
| $C_{1s,3}$ | -0.00245 | -0.00272 | -0.00237 | -0.00638 | -0.00748 | 0.00986 |
| $C_{1s,4}$ | 0.00341 | 0.00368 | 0.00348 | 0.00583 | 0.00684 | 0.00999 |
| $C_{1s,5}$ | -0.00079 | -0.00095 | -0.00096 | -0.00141 | -0.00142 | -0.00123 |
| $C_{1s,6}$ | 0.00035 | 0.00046 | 0.00045 | 0.00063 | 0.00069 | -0.00244 |
| $\epsilon_{2s}$ | -12.32139 | -12.83595 | -12.88297 | -13.61587 | -13.77364 | -14.17480 |
| Cusp | -17.98911 | -17.99026 | -17.99083 | -18.00607 | -18.02007 | -18.03109 |
| $C_{2s,1}$ | -0.24687 | -0.24712 | -0.24592 | -0.25697 | -0.25799 | -0.28557 |
| $C_{2s,2}$ | -0.12262 | -0.12272 | -0.12286 | -0.12721 | -0.13624 | -0.10624 |
| $C_{2s,3}$ | 0.12399 | 0.12384 | 0.12284 | 0.12539 | 0.08266 | 0.14049 |
| $C_{2s,4}$ | 0.95830 | 0.95863 | 0.95768 | 0.96574 | 1.00378 | 0.94875 |
| $C_{2s,5}$ | 0.00745 | 0.00727 | 0.00963 | 0.00599 | 0.02491 | 0.00724 |
| $C_{2s,6}$ | -0.00027 | -0.00033 | -0.00040 | 0.00090 | 0.00894 | 0.00010 |
| $\epsilon_{3s}$ | -1.27666 | -1.71130 | -1.81793 | -1.89215 | -1.87392 | -1.90793 |
| Cusp | -17.75815 | -17.75636 | -17.74072 | -17.72879 | -17.83920 | -17.75839 |
| $C_{3s,1}$ | 0.07681 | 0.07917 | 0.08033 | 0.08623 | 0.09084 | 0.09367 |
| $C_{3s,2}$ | 0.05492 | 0.05722 | 0.05843 | 0.06789 | 0.07238 | 0.05946 |
| $C_{3s,3}$ | 0.02678 | 0.03123 | 0.03317 | 0.05377 | 0.05842 | 0.04611 |
| $C_{3s,4}$ | -0.47508 | -0.49604 | -0.50585 | -0.56189 | -0.57408 | -0.54330 |
| $C_{3s,5}$ | 0.65610 | 0.60506 | 0.63491 | 0.60870 | 0.67677 | 0.59538 |
| $C_{3s,6}$ | 0.48338 | 0.53045 | 0.50004 | 0.54657 | 0.46372 | 0.55601 |
| $\epsilon_{2p}$ | -9.57061 | -10.08339 | -10.14938 | -11.10839 | -10.86733 | -11.71788 |
| Cusp | -8.60975 | -8.61881 | -8.62450 | -8.65542 | -8.67770 | -8.84569 |
| $C_{2p,1}$ | 0.19611 | 0.19240 | 0.19107 | 0.16434 | 0.16737 | 0.20753 |
| $C_{2p,2}$ | 0.82878 | 0.83062 | 0.83266 | 0.84393 | 0.85184 | 0.81457 |
| $C_{2p,3}$ | 0.01861 | 0.02242 | 0.02061 | 0.03805 | 0.02168 | 0.01642 |
| $C_{2p,4}$ | -0.00497 | -0.00547 | -0.00629 | 0.00967 | -0.00620 | -0.00428 |
| $\epsilon_{3p}$ | -0.59046 | -1.04550 | -1.03108 | -1.15874 | -1.15294 | -1.17519 |
| Cusp | -8.63989 | -8.63187 | -8.63848 | -8.62460 | -8.63667 | -8.86975 |
| $C_{3p,1}$ | -0.05049 | -0.05249 | -0.05178 | -0.04946 | -0.04559 | -0.05682 |
| $C_{3p,2}$ | -0.25002 | -0.27029 | -0.26961 | -0.31930 | -0.29823 | -0.27652 |
| $C_{3p,3}$ | 0.58087 | 0.55695 | 0.55483 | 0.58189 | 0.57570 | 0.56927 |
| $C_{3p,4}$ | 0.53221 | 0.54085 | 0.54469 | 0.52121 | 0.52995 | 0.53616 |

*States which are not the lowest of a symmetry species.

TABLE VIII. SCF Orbitals and Energies for $K^+$ and $n\ell$-hole States of $K^+$, Simple Basis Sets

| | $K^+(^1S)$ | $K^{++}(^2P)$ 3p-hole | $K^{++}(^2S)$ 3s-hole | $K^{++}(^2P)$* 2p-hole | $K^{++}(^2S)$* 2s-hole | $K^{++}(^2S)$* 1s-hole |
|---|---|---|---|---|---|---|
| E | -599.0159 | -597.8901 | -597.1025 | -587.6820 | -584.6705 | -466.4280 |
| V/T | -2.000002 | -2.000002 | -2.000002 | -2.000002 | -1.999998 | -1.999995 |
| $\zeta_1$(1s) | 20.222 | 20.200 | 20.339 | 19.998 | 20.006 | 19.464 |
| $\zeta_2$(2s) | 17.611 | 17.568 | 17.799 | 17.194 | 17.116 | 17.522 |
| $\zeta_3$(3s) | 11.812 | 11.804 | 11.603 | 11.868 | 11.962 | 12.155 |
| $\zeta_4$(2s) | 6.793 | 6.805 | 6.762 | 6.999 | 7.049 | 7.134 |
| $\zeta_5$(3s) | 3.502 | 3.520 | 3.599 | 3.787 | 3.660 | 3.814 |
| $\zeta_6$(3s) | 2.338 | 2.491 | 2.573 | 2.658 | 2.600 | 2.662 |
| $\zeta_1$(2p) | 11.838 | 11.880 | 11.890 | 12.210 | 12.228 | 11.965 |
| $\zeta_2$(2p) | 6.601 | 6.619 | 6.621 | 6.889 | 6.846 | 6.998 |
| $\zeta_3$(3p) | 3.239 | 3.290 | 3.300 | 3.441 | 3.453 | 3.561 |
| $\zeta_4$(3p) | 1.965 | 2.167 | 2.156 | 2.252 | 2.259 | 2.302 |
| $\epsilon_{1s}$ | -133.75073 | -134.40246 | -134.45380 | -136.06274 | -135.76712 | -143.07576 |
| Cusp | -18.95218 | -18.95205 | -18.95638 | -18.94390 | -18.95098 | -19.01711 |
| $C_{1s,1}$ | 0.88800 | 0.88948 | 0.88039 | 0.90332 | 0.90230 | 0.95351 |
| $C_{1s,2}$ | 0.13603 | 0.13446 | 0.14429 | 0.11956 | 0.12092 | 0.04811 |
| $C_{1s,3}$ | -0.00472 | -0.00528 | -0.00396 | -0.00904 | -0.00885 | 0.00779 |
| $C_{1s,4}$ | 0.00458 | 0.00501 | 0.00448 | 0.00720 | 0.00749 | 0.01140 |
| $C_{1s,5}$ | -0.00112 | -0.00136 | -0.00132 | -0.00185 | -0.00174 | -0.00128 |
| $C_{1s,6}$ | 0.00053 | 0.00070 | 0.00066 | 0.00089 | 0.00090 | -0.00243 |
| $\epsilon_{2s}$ | -14.70793 | -15.33966 | -15.37635 | -16.18405 | -16.34594 | -16.79222 |
| Cusp | -18.99464 | -19.00240 | -18.99354 | -19.00464 | -19.01649 | -19.00922 |
| $C_{2s,1}$ | -0.25518 | -0.25580 | -0.25269 | -0.26397 | -0.26285 | -0.29070 |
| $C_{2s,2}$ | -0.12988 | -0.13038 | -0.12747 | -0.14134 | -0.14610 | -0.12283 |
| $C_{2s,3}$ | 0.09466 | 0.09326 | 0.10736 | 0.07830 | 0.05739 | 0.08431 |
| $C_{2s,4}$ | 0.99545 | 0.99744 | 0.97862 | 1.02354 | 1.03674 | 1.01665 |
| $C_{2s,5}$ | 0.01053 | 0.01133 | 0.01083 | 0.01144 | 0.02561 | 0.01163 |
| $C_{2s,6}$ | -0.00135 | -0.00225 | -0.00055 | -0.00115 | 0.00869 | -0.00153 |
| $\epsilon_{3s}$ | -1.96364 | -2.47755 | -2.58857 | -2.68729 | -2.66576 | -2.71209 |
| Cusp | -18.81626 | -18.82281 | -18.73490 | -18.82718 | -18.88418 | -18.86195 |
| $C_{3s,1}$ | 0.08380 | 0.08639 | 0.08671 | 0.09277 | 0.09651 | 0.10010 |
| $C_{3s,2}$ | 0.06244 | 0.06489 | 0.06623 | 0.07783 | 0.08153 | 0.06895 |
| $C_{3s,3}$ | 0.04043 | 0.04354 | 0.05050 | 0.06891 | 0.07410 | 0.06040 |
| $C_{3s,4}$ | -0.52140 | -0.53996 | -0.55866 | -0.60641 | -0.62185 | -0.58590 |
| $C_{3s,5}$ | 0.63334 | 0.62015 | 0.57039 | 0.56953 | 0.62156 | 0.58244 |
| $C_{3s,6}$ | 0.50598 | 0.51587 | 0.57106 | 0.58382 | 0.52239 | 0.56650 |
| $\epsilon_{2p}$ | -11.73792 | -12.36825 | -12.42694 | -13.48136 | -13.21598 | -14.14875 |
| Cusp | -9.14221 | -9.14897 | -9.15299 | -9.18073 | -9.20343 | -9.36415 |
| $C_{2p,1}$ | 0.18371 | 0.18054 | 0.18030 | 0.15466 | 0.15745 | 0.19632 |
| $C_{2p,2}$ | 0.83783 | 0.83920 | 0.84055 | 0.85107 | 0.85924 | 0.82317 |
| $C_{2p,3}$ | 0.02070 | 0.02456 | 0.02220 | 0.03860 | 0.02333 | 0.01796 |
| $C_{2p,4}$ | -0.00591 | -0.00658 | -0.00725 | 0.00778 | -0.00728 | -0.00510 |
| $\epsilon_{3p}$ | -1.17044 | -1.71127 | -1.68849 | -1.85283 | -1.84601 | -1.88080 |
| Cusp | -9.14340 | -9.14264 | -9.14979 | -9.13004 | -9.14083 | -9.37069 |
| $C_{3p,1}$ | -0.05010 | -0.05196 | -0.05152 | -0.04788 | -0.04447 | -0.05596 |
| $C_{3p,2}$ | -0.28036 | -0.29883 | -0.29718 | -0.34421 | -0.32398 | -0.30266 |
| $C_{3p,3}$ | 0.56462 | 0.54277 | 0.54510 | 0.58046 | 0.57500 | 0.56238 |
| $C_{3p,4}$ | 0.53895 | 0.55028 | 0.54969 | 0.51866 | 0.52659 | 0.53909 |

*States which are not the lowest of a symmetry species.

The accurate basis sets for the states of the light atoms (fluorine, neon, and sodium) are composed of five s and four p basis functions. The one exception is the basis set for $F^-$, which is composed of six x and five p basis functions.

The accurate basis sets for the states of the heavier atoms (chlorine, argon, and potassium) are composed of seven s and either six or seven p basis functions. The seven p sets used three basis functions to represent the outer loop of the 3p orbital. The addition of a third basis function to represent this loop caused only a small improvement in the total energy. For most of the states of $K^{++}$, a third basis function did not cause any improvement in the total energy. Only two basis functions were used to represent the loop for these states.

The simple basis sets for the light atoms are composed of four s and three p basis functions. Two basis functions are used to represent each loop of the s orbitals. The simple basis sets for the heavier atoms are composed of six s and four p basis functions; two basis functions are used to represent each loop of the orbitals. The automatic exponent variation procedures of the SCF program converge quickly to the optimum values of the exponents of the simple basis sets; almost no manual examination of the intermediate results, and consequent readjustment of the exponent variation parameters, are required. Thus, the calculation of the simple basis set functions is extremely automatic and requires the use of little human or machine time. Of the simple basis set SCF functions, the two which give the poorest approximations to the exact HF functions are the functions for the negative ions $F^-$ and $Cl^-$. (The simple basis sets for the light atoms were called nominal basis sets in an earlier paper.(9) The reasons for the use of this name were explained in that paper.)

The optimum values of the exponents are not determined in all cases to the number of significant figures given in Tables I-VIII. This is especially true for the large exponents of the basis functions used to represent inner loops, and for the large, accurate, basis sets. Some of the exponents used to represent a loop are better determined than others. The exponents of the dominant basis functions (usually the basis functions with the largest vector coefficients $C_{n\ell,p}$) are often well-determined once the exponents of the less important basis functions are fixed. The largest exponents of the accurate basis sets of the heavier atoms were rounded. The largest exponents of the p basis functions of some of the states of $Ne^+$ and $Na^{++}$ were also rounded to simple values. Beyond this, we did not make a systematic attempt to round any of the other exponents but used them, rounded to three decimal places, as they were obtained from the SCF computer program. When exponents were rounded, the vector coefficients given are those determined from SCF calculations made using the rounded values of the exponents.

## B. Accuracy of the SCF Wave Functions

Estimates were made of the effect of round-off errors on the SCF calculations. As a part of the round-off error, we include the extent to which the results are not self-consistent solutions of the matrix HF equations. Our estimates of round-off error are based, primarily, on information gained in the following ways:

1. The examination of the convergence thresholds, for diagonalization and self-consistency met by the SCF vector coefficients. These thresholds are part of the output of the computer program and are also set automatically by the program depending on the features of the calculation being performed.(4) Unfortunately, our experience indicates that these thresholds give a low estimate of the effects of round-off errors.

2. The comparison of the results of SCF calculations performed on the IBM 704 and on the IBM 7094. The most important difference between the 704 and 7094 programs is that in the 7094 program the results of floating-point addition and multiplication are rounded, while in the 704 program they are not. Thus a comparison of the results of SCF calculations, performed on the 704 and 7094, should provide an estimate, most likely on the high side, of the effect of rounding errors on the 7094 results.

3. The comparison of the results of two SCF calculations, both performed on the 7094 and using the same basis set, but with somewhat different initial approximations for the SCF eigenvectors.

For the calculations performed with small basis sets, viz., the simple sets for the heavier atoms (chlorine, argon, and potassium) and both the simple and accurate sets for the lighter atoms (fluorine, neon, and sodium), the estimates of round-off errors are the following: The round-off error in the total energy and V/T is probably less than or equal to five units in the eighth significant figure. For those states for which the total energy is just larger than 100 Hartrees, the round-off error in the total energy is probably less than two units in the eighth significant figure. The round-off error in the $\epsilon_{n\ell}$'s and $C_{n\ell,p}$'s is probably less than or equal to one unit in the fifth decimal place (that is, one unit in the last figure given for these quantities in Tables I-VIII). The round-off error in the cusps is usually less than one unit in the fifth decimal place, but in some cases is probably about three or four units in the fifth decimal place.

For calculations with the accurate basis sets for the heavier atoms, the estimates of round-off error are the following: The round-off error in the total energy is probably less than four to eight units in the eighth significant figure. The round-off error in V/T is usually about five units in the eighth significant figure, but in a few cases it is as large as four in the seventh significant figure. The round-off error for the $\epsilon_{n\ell}$'s and cusps varies depending on the orbital considered (1s, 2s, 2p, etc.), but in any case is no more than one or two units in the fourth decimal place. The round-off error for the $C_{n\ell,p}$'s for s orbitals is about one unit in the fifth decimal place, and for p orbitals is less than one unit in the fourth place.

The round-off error is larger for the vector coefficients of p orbitals because the p basis functions form a more nearly linearly dependent set than the s basis functions. The diagonalization procedures lose accuracy as the basis set becomes linearly dependent. For example, for the accurate basis set for neutral argon, the determinant of the overlap matrix of the p basis functions is $0.5 \times 10^{-6}$; for the s basis functions it is $5.3 \times 10^{-6}$, a factor of 10 larger. But, because of the redundancy of the p basis functions, the round-off errors in the vector coefficients may not have a large effect on the numerical values of the p orbitals.

Although the vectors given in Tables I-VIII may not be SCF eigenvectors to the number of figures given, they do form an orthonormal set to the number of figures given.

It is important to obtain reliable estimates of the accuracy of the analytic SCF wave functions. By accuracy of the analytic functions we mean how closely they represent the exact HF solutions. Information on the accuracy of the analytic functions may be obtained in the following ways:

1. The comparison of analytic functions with solutions obtained by direct numerical integration. This method has limited usefulness; first, because numerical solutions are often not available and, second, because accurate analytic functions are often better than the available numerical solutions.

2. The comparison of different, good, analytic functions for the same state, calculated independently by different workers or with a different choice of principal quantum numbers for the basis functions, but with very nearly the same total energy. These calculations are not likely to have the same systematic errors because of individual peculiarities in the choice and optimization of the basis functions. Thus, it is reasonable that the differences between the results of these calculations should represent the random error of functions with this total energy. These differences provide a good basis for estimating the accuracy of the functions.

3. The examination of the convergence of the properties of the SCF functions obtained in the process of building up the basis set from a small set to the final accurate set. This method is very powerful when the basis set is <u>completely</u> reoptimized at each step of the build-up so that the effects of systematic errors on the choice of basis functions to represent a

loop are minimized. These techniques and their application to first-row atoms are discussed elsewhere.(9)

The cusp is not useful as a guide to the accuracy of any fairly good analytic SCF function. For all but very small basis sets, the cusp condition is satisfied well enough, if optimized basis functions are used, to insure against unreasonable behavior at the origin. This is because an analytic SCF radial function $P_{n\ell}(r)$, $P_{n\ell}(r) = rF_{n\ell}(r) = r\Sigma R_{\ell p}(r)C_{n\ell,p}$, goes near the origin as

$$P_{n\ell}(r) = A_0(n\ell)r^{\ell+1}[1 + (Cusp_{n\ell})r + 0(r^2)]. \tag{13}$$

The dominant term in this expansion is $A_0(n\ell)$, not the cusp, and $P_{n\ell}$ is not overly sensitive to errors in the cusp.

Fortunately, it is not necessary to apply the tests described above to every analytic SCF function that is calculated. When the SCF functions of a series of similar states have been calculated in a systematic way, as described in Section III of this paper, the accuracy of each function in the series may be inferred from careful estimates of the accuracy of the functions of only a few states. One must take some precautions when making these inferences of estimates of accuracy. It is important, for example, to remember that it may be more difficult to determine more diffuse orbitals, e.g., orbitals of negative ions, as accurately as less diffuse ones.

Tables IX-XII present comparisons of the results of several HF calculations of Ne, $F^-$, Ar, and $Cl^-$ with the results obtained with our accurate basis set functions. In each case, we give comparisons with results obtained by direct numerical integration of the HF equations;* and, except for $Cl^-$, we also give comparisons with analytic SCF functions with very nearly the same energy as our accurate-set functions. The analytic functions whose total SCF energies differ only in the eighth significant figure are grouped together with the accurate-set function at the left of the tables. Comparisons between these functions give information of the type 2 above. We have included, for each case, comparison with the results obtained with the simple basis set functions so that the accuracy of these functions may be determined.

For Ne and $F^-$, we include comparisons with the analytic SCF calculations of Allen,(36) and for Ar and $Cl^-$, with the analytic SCF calculations of Watson and Freeman.(37) These calculations were performed without using techniques for the automatic optimization of the exponents of the basis functions.

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*For numerical HF calculations of Ne, $F^-$, Ar, and $Cl^-$, see Refs. 32, 33, 34, and 35, respectively.

TABLE IX. Comparison of Several Hartree-Fock Calculations of Neon

(Values are in a.u.)

| | | This Calculation Accurate Set | Fixed Cusp Set[a] | Clementi[b] | Worsley[c] (Numerical Integration) | This Calculation Simple Set | Allen[d] |
|---|---|---|---|---|---|---|---|
| $E$ | | -128.54709 | -128.54703 | -128.54701 | . . . . . . . | -128.54648 | -128.54319 |
| $\Delta E$ | | 0 | -0.00006 | -0.00008 | . . . . . | -0.00061 | -0.00390 |
| $\epsilon_{1s}$ | | -32.77233 | -32.77229 | -32.77277 | $-32.77_5$ | -32.77162 | -32.76740 |
| $\Delta\epsilon_{1s}$ | | 0 | -0.00004 | +0.00044 | $+0.00_3$ | -0.00071 | -0.00493 |
| $\mathrm{Cusp}_{1s}$ | | -10.0250 | -10.0000 | -10.0049 | . . . . . | -10.0101 | -9.9994 |
| $\Delta\mathrm{Cusp}_{1s}$ | | +0.0250 | . . . . . | +0.0049 | . . . . . | +0.0101 | -0.0006 |
| $\lvert A_o(1s)\rvert$ | | 60.777 | 60.741 | 60.750 | 60.77 | 60.761 | 60.746 |
| $\Delta\lvert A_o(1s)\rvert$ | | -0.01 | +0.03 | +0.02 | 0 | +0.01 | +0.02 |
| $\langle r\rangle_{1s}$ | | 0.15763 | 0.15763 | 0.15763 | . . . . . | 0.15763 | 0.15764 |
| $\Delta\langle r\rangle_{1s}$ | | 0 | 0.00000 | 0.00000 | . . . . . | 0.00000 | -0.00001 |
| $\langle r^2\rangle_{1s}$ | | 0.03347 | 0.03347 | 0.03347 | . . . . . | 0.03347 | 0.03347 |
| $\Delta\langle r^2\rangle_{1s}$ | | 0 | 0.00000 | 0.00000 | . . . . . | 0.00000 | 0.00000 |
| $[\int(\Delta P_{1s})^2]^{\frac{1}{2}}$ | | 0 | 0.0005 | 0.0004 | . . . . . | 0.0005 | 0.0006 |
| $\lvert\Delta P_{1s}\rvert_{max}$ | $0 \leq r < \infty$ | 0 | 0.0002 | 0.0003 | 0.003 | 0.0004 | 0.0005 |
| $\epsilon_{2s}$ | | -1.93031 | -1.93031 | -1.93048 | -1.933 | -1.92975 | -1.92592 |
| $\Delta\epsilon_{2s}$ | | 0 | 0.00000 | +0.00017 | +0.003 | -0.00056 | -0.00439 |
| $\mathrm{Cusp}_{2s}$ | | -10.0535 | -10.0000 | -10.0052 | . . . . . | -10.0136 | -10.3010 |
| $\Delta\mathrm{Cusp}_{2s}$ | | +0.0535 | . . . . . | +0.0052 | . . . . . | +0.0136 | +0.3010 |
| $\lvert A_o(2s)\rvert$ | | 14.280 | 14.253 | 14.264 | 14.27 | 14.269 | 14.344 |
| $\Delta\lvert A_o(2s)\rvert$ | | -0.01 | +0.02 | +0.01 | 0 | 0.00 | -0.07 |
| $\langle r\rangle_{2s}$ | | 0.89209 | 0.89207 | 0.89216 | . . . . . | 0.89135 | 0.89267 |
| $\Delta\langle r\rangle_{2s}$ | | 0 | +0.00002 | -0.00007 | . . . . . | +0.00074 | -0.00058 |
| $\langle r^2\rangle_{2s}$ | | 0.96694 | 0.96691 | 0.96735 | . . . . . | 0.96359 | 0.96964 |
| $\Delta\langle r^2\rangle_{2s}$ | | 0 | +0.00003 | -0.00041 | . . . . . | +0.00335 | -0.00270 |
| $[\int(\Delta P_{2s})^2]^{\frac{1}{2}}$ | | 0 | 0.0014 | 0.0015 | . . . . . | 0.0054 | 0.0061 |
| $\lvert\Delta P_{2s}\rvert_{max}$ | $0 \leq r < 1.0$ | 0 | 0.0002 | 0.0004 | 0.0003 | 0.0015 | 0.0023 |
| | $1.0 \leq r < \infty$ | 0 | 0.0009 | 0.0012 | 0.001 | 0.0046 | 0.0046 |
| $\epsilon_{2p}$ | | -0.85034 | -0.85033 | -0.85048 | $-0.852_5$ | -0.84974 | -0.84610 |
| $\Delta\epsilon_{2p}$ | | 0 | -0.00001 | +0.00014 | $+0.002_2$ | -0.00060 | -0.00424 |
| $\mathrm{Cusp}_{2p}$ | | -5.0003 | -5.0000 | -5.0000 | . . . . . | -4.6751 | -4.7356 |
| $\Delta\mathrm{Cusp}_{2p}$ | | +0.0003 | . . . . . | 0.0000 | . . . . . | -0.3249 | -0.2644 |
| $\lvert A_o(2p)\rvert$ | | 27.804 | 27.732 | 27.861 | 27.87 | 27.159 | 27.479 |
| $\Delta\lvert A_o(2p)\rvert$ | | +0.07 | +0.14 | +0.01 | 0 | +0.71 | +0.39 |
| $\langle r\rangle_{2p}$ | | 0.96518 | 0.96519 | 0.96537 | . . . . . | 0.96477 | 0.96489 |
| $\Delta\langle r\rangle_{2p}$ | | 0 | -0.00001 | -0.00019 | . . . . . | +0.00041 | +0.00029 |
| $\langle r^2\rangle_{2p}$ | | 1.22789 | 1.22787 | 1.22901 | . . . . . | 1.22516 | 1.23800 |
| $\Delta\langle r^2\rangle_{2p}$ | | 0 | +0.00002 | -0.00112 | . . . . . | +0.00273 | -0.01011 |
| $[\int(\Delta P_{2p})^2]^{\frac{1}{2}}$ | | 0 | 0.0010 | 0.0017 | . . . . . | 0.0037 | 0.0186 |
| $\lvert\Delta P_{2p}\rvert_{max}$ | $0 \leq r < 1.0$ | 0 | 0.0002 | 0.0006 | 0.0002 | 0.0011 | 0.0063 |
| | $1.0 \leq r < \infty$ | 0 | 0.0006 | 0.0011 | 0.004 | 0.0026 | 0.0102 |

[a] P. S. Bagus, T. L. Gilbert, C. C. J. Roothaan, and H. D. Cohen (see Ref. 9).

[b] E. Clementi, C. C. J. Roothaan, and M. Yoshimine (see Ref. 7).

[c] B. H. Worsley (see Ref. 32).

[d] L. C. Allen (see Ref. 36).

TABLE X. Comparison of Several Hartree-Fock Calculations of $F^-$

(Values are in a.u.)

| | | This Calculation Accurate Set | Fixed Cusp Set[a] | Froese[b] (Numerical Integration) | Clementi[c] | Allen[d] | This Calculation Simple Set |
|---|---|---|---|---|---|---|---|
| $E$ | | -99.459440 | -99.459444 | . . . . | -99.459363 | -99.458879 | -99.457854 |
| $\Delta E$ | | 0 | +0.000004 | . . . . | -0.000077 | -0.000561 | -0.001586 |
| $\epsilon_{1s}$ | | -25.82961 | -25.82961 | $-25.822_5$ | -25.82944 | -25.82957 | -25.82687 |
| $\Delta\epsilon_{1s}$ | | 0 | +0.00000 | $-0.007_1$ | -0.00017 | -0.00004 | -0.00274 |
| $\mathrm{Cusp}_{1s}$ | | -9.0240 | -9.0000 | . . . . | -9.0174 | -9.0055 | -9.0124 |
| $\Delta\mathrm{Cusp}_{1s}$ | | +0.0240 | . . . . . | . . . . | +0.0174 | +0.0055 | +0.0124 |
| $\lvert A_o(1s)\rvert$ | | 51.724 | 51.702 | 51.705 | 51.717 | 51.703 | 51.713 |
| $\Delta\lvert A_o(1s)\rvert$ | | -0.019 | +0.003 | 0 | -0.012 | +0.002 | -0.008 |
| $\langle r\rangle_{1s}$ | | 0.17576 | 0.17576 | . . . . | 0.17576 | 0.17577 | 0.17575 |
| $\Delta\langle r\rangle_{1s}$ | | 0 | 0.00000 | . . . . | 0.00000 | -0.00001 | +0.00001 |
| $\langle r^2\rangle_{1s}$ | | 0.04162 | 0.04162 | . . . . | 0.04162 | 0.04162 | 0.04161 |
| $\Delta\langle r^2\rangle_{1s}$ | | 0 | 0.00000 | . . . . | 0.00000 | 0.00000 | +0.00001 |
| $[\int(\Delta P_{1s})^2]^{\frac{1}{2}}$ | | 0 | ≤0.0002 | . . . . | 0.0004 | 0.0004 | 0.0006 |
| $\lvert\Delta P_{1s}\rvert_{max}$ | $0 \leq r < \infty$ | 0 | 0.0002 | 0.0003 | 0.0002 | 0.0004 | 0.0005 |
| $\epsilon_{2s}$ | | -1.07458 | -1.07458 | $-1.076_5$ | -1.07435 | -1.07468 | -1.07236 |
| $\Delta\epsilon_{2s}$ | | 0 | 0.00000 | $+0.001_9$ | -0.00023 | +0.00010 | -0.00222 |
| $\mathrm{Cusp}_{2s}$ | | -9.0678 | -9.0000 | . . . . | -9.0345 | -9.2576 | -9.0753 |
| $\Delta\mathrm{Cusp}_{2s}$ | | +0.0678 | . . . . . | . . . . | +0.0345 | +0.2576 | +0.0753 |
| $\lvert A_o(2s)\rvert$ | | 11.683 | 11.667 | 11.669 | 11.670 | 11.729 | 11.688 |
| $\Delta\lvert A_o(2s)\rvert$ | | -0.014 | +0.002 | 0 | -0.001 | -0.060 | -0.019 |
| $\langle r\rangle_{2s}$ | | 1.03555 | 1.03556 | . . . . | 1.03540 | 1.03617 | 1.03333 |
| $\Delta\langle r\rangle_{2s}$ | | 0 | -0.00001 | . . . . | +0.00015 | -0.00062 | +0.00222 |
| $\langle r^2\rangle_{2s}$ | | 1.31886 | 1.31903 | . . . . | 1.31776 | 1.32219 | 1.30703 |
| $\Delta\langle r^2\rangle_{2s}$ | | 0 | -0.00017 | . . . . | +0.00110 | -0.00333 | +0.01183 |
| $[\int(\Delta P_{2s})^2]^{\frac{1}{2}}$ | | 0 | 0.0009 | . . . . | 0.0027 | 0.0035 | 0.0118 |
| $\lvert\Delta P_{2s}\rvert_{max}$ | $0 \leq r < 1.5$ | 0 | 0.0003 | 0.0005 | 0.0009 | 0.0015 | 0.0024 |
| | $1.5 \leq r < \infty$ | 0 | 0.0006 | 0.0005 | 0.0018 | 0.0026 | 0.0088 |
| $\epsilon_{2p}$ | | -0.18098 | -0.18098 | $-0.181_5$ | -0.18079 | -0.18122 | -0.17886 |
| $\Delta\epsilon_{2p}$ | | 0 | 0.00000 | $+0.000_5$ | -0.00019 | +0.00024 | -0.00212 |
| $\mathrm{Cusp}_{2p}$ | | -4.5322 | -4.5000 | . . . . | -4.4282 | -4.1523 | -4.0292 |
| $\Delta\mathrm{Cusp}_{2p}$ | | +0.0322 | . . . . . | . . . . . | -0.0718 | -0.3477 | -0.4708 |
| $\lvert A_o(2p)\rvert$ | | 18.861 | 18.882 | 18.849 | 18.740 | 18.268 | 18.017 |
| $\Delta\lvert A_o(2p)\rvert$ | | -0.012 | -0.033 | 0 | +0.109 | +0.581 | +0.832 |
| $\langle r\rangle_{2p}$ | | 1.25556 | 1.25557 | . . . . | 1.25512 | 1.25604 | 1.25206 |
| $\Delta\langle r\rangle_{2p}$ | | 0 | -0.00001 | . . . . | +0.00044 | -0.00048 | +0.00350 |
| $\langle r^2\rangle_{2p}$ | | 2.20956 | 2.20971 | . . . . | 2.20516 | 2.21748 | 2.17892 |
| $\Delta\langle r^2\rangle_{2p}$ | | 0 | -0.00015 | . . . . | +0.00440 | -0.00792 | +0.03064 |
| $[\int(\Delta P_{2p})^2]^{\frac{1}{2}}$ | | 0 | 0.0007 | . . . . | 0.0024 | 0.0076 | 0.0121 |
| $\lvert\Delta P_{2p}\rvert_{max}$ | $0 \leq r < 1.5$ | 0 | 0.0002 | 0.0002 | 0.0002 | 0.0012 | 0.0021 |
| | $1.5 \leq r < \infty$ | 0 | $0.0003_5$ | 0.0005 | 0.0013 | 0.0034 | 0.0067 |

[a] P. S. Bagus, T. L. Gilbert, C. C. J. Roothaan, and H. Cohen (see Ref. 9).

[b] C. Froese (see Ref. 33).

[c] E. Clementi and A. D. McLean (see Ref. 38).

[d] L. C. Allen (see Ref. 36).

TABLE XI. Comparison of Several Hartree-Fock Calculations of Argon

(Values are in a.u.)

| | | This Calculation Accurate Set | Alternate[a] Large Set 8s and 7p | Malli[b] (Fixed Cusp Set) | Hartree[c] (Numerical Integration) | Clementi[d] | This Calculation Simple Set | Watson and Freeman[e] |
|---|---|---|---|---|---|---|---|---|
| $E$ | | -526.81746 | -526.81745 | -526.81743 | . . . . . | -526.81707 | -526.81553 | -526.81463 |
| $\Delta E$ | | 0 | -0.00001 | -0.00003 | . . . . . | -0.00039 | -0.00193 | -0.00283 |
| $\epsilon_{1s}$ | | 118.61014 | -118.61042 | -118.61030 | -118.6 | -118.60987 | -118.60817 | -118.60950 |
| $\Delta\epsilon_{1s}$ | | 0 | +0.00028 | +0.00016 | 0.0 | -0.00027 | -0.00197 | -0.00064 |
| $\mathrm{Cusp}_{1s}$ | | -18.0037 | -18.0063 | -18.0000 | . . . . . | -18.0298 | -17.9582 | -17.9727 |
| $\Delta\mathrm{Cusp}_{1s}$ | | +0.0037 | +0.0063 | . . . . . | . . . . . | +0.0298 | -0.0418 | -0.0273 |
| $\lvert A_0(1s)\rvert$ | | 148.87 | 148.88 | 148.85 | 148.8 | 148.92 | 148.77 | 148.81 |
| $\Delta\lvert A_0(1s)\rvert$ | | -0.1 | -0.1 | 0.0 | 0 | -0.1 | 0.0 | 0.0 |
| $\langle r\rangle_{1s}$ | | 0.08610 | 0.08610 | 0.08610 | . . . . . | 0.08610 | 0.08611 | 0.08610 |
| $\Delta\langle r\rangle_{1s}$ | | 0 | 0.00000 | 0.00000 | . . . . . | 0.00000 | -0.00001 | 0.00000 |
| $\langle r^2\rangle_{1s}$ | | 0.00996 | 0.00996 | 0.00996 | 0.010 | 0.00996 | 0.00996 | 0.00996 |
| $\Delta\langle r^2\rangle_{1s}$ | | 0 | 0.00000 | 0.00000 | 0.000 | 0.00000 | 0.00000 | 0.00000 |
| $[\int(\Delta P_{1s})^2]^{\frac{1}{2}}$ | | 0 | ≤0.0001 | ≤0.0002 | . . . . . | ≤0.0003 | 0.0005 | 0.0004 |
| $\lvert\Delta P_{1s}\rvert_{\max}$ | $0 \leq r < \infty$ | 0 | 0.0001 | 0.0002 | 0.007 | 0.0003 | 0.0008 | 0.0004 |
| $\epsilon_{2s}$ | | -12.32193 | -12.32220 | -12.32214 | $-12.3_3$ | -12.32150 | -12.32139 | -12.32141 |
| $\Delta\epsilon_{2s}$ | | 0 | +0.00027 | +0.00021 | $+0.0_1$ | -0.00043 | -0.00054 | -0.00052 |
| $\mathrm{Cusp}_{2s}$ | | -17.9965 | -18.0049 | -18.0000 | . . . . . | -17.9940 | -17.9891 | -18.2048 |
| $\Delta\mathrm{Cusp}_{2s}$ | | -0.0035 | +0.0049 | . . . . . | . . . . . | -0.0060 | -0.0109 | +0.2048 |
| $\lvert A_0(2s)\rvert$ | | 42.257 | 42.266 | 42.244 | 42.25 | 42.254 | 42.252 | 42.276 |
| $\Delta\lvert A_0(2s)\rvert$ | | -0.01 | -0.02 | +0.01 | 0 | 0.00 | 0.00 | -0.03 |
| $\langle r\rangle_{2s}$ | | 0.41228 | 0.41227 | 0.41229 | . . . . . | 0.41228 | 0.41231 | 0.41228 |
| $\Delta\langle r\rangle_{2s}$ | | 0 | +0.00001 | -0.00001 | . . . . . | 0.00000 | -0.00003 | 0.00000 |
| $\langle r^2\rangle_{2s}$ | | 0.20123 | 0.20122 | 0.20123 | 0.201 | 0.20122 | 0.20125 | 0.20122 |
| $\Delta\langle r^2\rangle_{2s}$ | | 0 | +0.00001 | 0.00000 | 0.000 | +0.00001 | -0.00002 | +0.00001 |
| $[\int(\Delta P_{2s})^2]^{\frac{1}{2}}$ | | 0 | 0.0005 | 0.0004 | . . . . . | 0.0008 | 0.0005 | 0.0006 |
| $\lvert\Delta P_{2s}\rvert_{\max}$ | $0 \leq r < 0.35$ | 0 | 0.0002 | 0.0002 | 0.002 | 0.0002 | 0.0004 | 0.0003 |
| | $0.35 \leq r < \infty$ | 0 | 0.0005 | 0.0002 | 0.002 | 0.0006 | 0.0006 | 0.0005 |
| $\epsilon_{3s}$ | | -1.27725 | -1.27734 | -1.27735 | $-1.277_5$ | -1.27692 | -1.27666 | -1.27649 |
| $\Delta\epsilon_{3s}$ | | 0 | +0.00009 | +0.00010 | $+0.000_2$ | -0.00033 | -0.00059 | -0.00076 |
| $\mathrm{Cusp}_{3s}$ | | -17.9689 | -17.9517 | -18.0000 | . . . . . | -18.0976 | -17.7582 | -17.9798 |
| $\Delta\mathrm{Cusp}_{3s}$ | | -0.0311 | -0.0483 | . . . . . | . . . . . | +0.0976 | -0.2418 | -0.0202 |
| $\lvert A_0(3s)\rvert$ | | 13.199 | 13.197 | 13.199 | 13.21 | 13.222 | 13.146 | 13.201 |
| $\Delta\lvert A_0(3s)\rvert$ | | +0.01 | +0.01 | +0.01 | 0 | -0.01 | +0.06 | +0.01 |
| $\langle r\rangle_{3s}$ | | 1.42196 | 1.42228 | 1.42192 | . . . . . | 1.42256 | 1.42218 | 1.42252 |
| $\Delta\langle r\rangle_{3s}$ | | 0 | -0.00032 | +0.00004 | . . . . . | -0.00060 | -0.00022 | -0.00056 |
| $\langle r^2\rangle_{3s}$ | | 2.34912 | 2.35086 | 2.34888 | 2.348 | 2.35144 | 2.34981 | 2.35372 |
| $\Delta\langle r^2\rangle_{3s}$ | | 0 | -0.00174 | +0.00024 | +0.001 | -0.00232 | -0.00069 | -0.00460 |
| $[\int(\Delta P_{3s})^2]^{\frac{1}{2}}$ | | 0 | 0.0009 | 0.0004 | . . . . . | 0.0025 | 0.0006 | 0.0059 |
| $\lvert\Delta P_{3s}\rvert_{\max}$ | $0 \leq r < 1.2$ | 0 | 0.0002 | 0.0002 | 0.001 | 0.0009 | 0.0007 | 0.0003 |
| | $1.2 \leq r < \infty$ | 0 | 0.0006 | 0.0002 | 0.001 | 0.0021 | 0.0004 | 0.0042 |

TABLE XI. Continued.

(Values are in a.u.)

| | | This Calculation Accurate Set | Alternate[a] Large Set 8s and 7p | Malli[b] (Fixed Cusp Set) | Hartree[c] (Numerical Integration) | Clementi[d] | This Calculation Simple Set | Watson and Freeman[e] |
|---|---|---|---|---|---|---|---|---|
| $\epsilon_{2p}$ | | -9.57127 | -9.57152 | -9.57146 | $-9.57_5$ | -9.57083 | -9.57061 | -9.57072 |
| $\Delta\epsilon_{2p}$ | | 0 | +0.00025 | +0.00019 | $+0.00_4$ | -0.00044 | -0.00066 | -0.00055 |
| $\text{Cusp}_{2p}$ | | -8.9259 | -8.9577 | -9.0000 | . . . . . | -8.9011 | -8.6098 | -8.7697 |
| $\Delta\text{Cusp}_{2p}$ | | -0.0741 | -0.0423 | . . . . . | . . . . . | -0.0989 | -0.3902 | -0.2303 |
| $\lvert A_o(2p)\rvert$ | | 181.89 | 182.07 | 182.14 | $182.3_5$ | 181.81 | 179.21 | 180.54 |
| $\Delta\lvert A_o(2p)\rvert$ | | $+0.4_6$ | $+0.2_8$ | $+0.2_1$ | 0 | $+0.5_4$ | $+3.1_5$ | $+1.8_1$ |
| $\langle r\rangle_{2p}$ | | 0.37533 | 0.37533 | 0.37533 | . . . . . | 0.37529 | 0.37527 | 0.37536 |
| $\Delta\langle r\rangle_{2p}$ | | 0 | 0.00000 | 0.00000 | . . . . . | +0.00004 | +0.00006 | -0.00003 |
| $\langle r^2\rangle_{2p}$ | | 0.17434 | 0.17434 | 0.17434 | 0.174 | 0.17430 | 0.17427 | 0.17437 |
| $\Delta\langle r^2\rangle_{2p}$ | | 0 | 0.00000 | 0.00000 | 0.000 | +0.00004 | +0.00007 | -0.00003 |
| $[\int(\Delta P_{2p})^2]^{\frac{1}{2}}$ | | 0 | 0.0005 | 0.0004 | . . . . . | 0.0009 | 0.0028 | 0.0016 |
| $\lvert\Delta P_{2p}\rvert_{max}$ | $0 \leq r < \infty$ | 0 | 0.0002 | 0.0003 | 0.002 | 0.0007 | 0.0026 | 0.0014 |
| $\epsilon_{3p}$ | | -0.59092 | -0.59102 | -0.59099 | $-0.590_5$ | -0.59071 | -0.59046 | -0.58997 |
| $\Delta\epsilon_{3p}$ | | 0 | +0.00010 | +0.00007 | $-0.000_4$ | -0.00021 | -0.00046 | -0.00095 |
| $\text{Cusp}_{3p}$ | | -8.8809 | -8.9471 | -9.0000 | . . . . . | -8.9216 | -8.6399 | -9.1924 |
| $\Delta\text{Cusp}_{3p}$ | | -0.1191 | -0.0529 | . . . . . | . . . . . | -0.0784 | -0.3601 | +0.1924 |
| $\lvert A_o(3p)\rvert$ | | 50.707 | 50.824 | 50.804 | 50.97 | 50.790 | 50.018 | 51.638 |
| $\Delta\lvert A_o(3p)\rvert$ | | +0.26 | +0.15 | +0.17 | 0 | +0.18 | +0.95 | -0.67 |
| $\langle r\rangle_{3p}$ | | 1.66276 | 1.66289 | 1.66298 | . . . . . | 1.66181 | 1.66156 | 1.66343 |
| $\Delta\langle r\rangle_{3p}$ | | 0 | -0.00013 | -0.00022 | . . . . . | +0.00095 | +0.00120 | -0.00067 |
| $\langle r^2\rangle_{3p}$ | | 3.30917 | 3.31003 | 3.31087 | 3.312 | 3.30105 | 3.29947 | 3.32762 |
| $\Delta\langle r^2\rangle_{3p}$ | | 0 | -0.00086 | -0.00170 | -0.003 | +0.00812 | +0.00970 | -0.01845 |
| $[\int(\Delta P_{3p})^2]^{\frac{1}{2}}$ | | 0 | 0.0006 | 0.0019 | . . . . . | 0.0051 | 0.0051 | 0.0179 |
| $\lvert\Delta P_{3p}\rvert_{max}$ | $0 \leq r < 1.3$ | 0 | 0.0003 | 0.0002 | 0.001 | 0.0009 | 0.0007 | 0.0025 |
| | $1.3 \leq r < \infty$ | 0 | 0.0004 | 0.0011 | 0.001 | 0.0032 | 0.0033 | 0.0096 |

[a] P. S. Bagus (unpublished).

[b] G. L. Malli (to be published).

[c] D. R. Hartree and W. Hartree (see Ref. 34) solved the SCF equations with exchange only for the 3s and 3p wave functions; the 1s, 2s, and 2p wave functions with exchange were obtained from the functions without exchange and interpolation between the values for $Ca^{++}$, $K^+$, and $Cl^-$.

[d] E. Clementi (see Ref. 39). Details of the function are not published in Clementi's paper but are available at the Library of Congress (see Ref. 40).

[e] R. E. Watson and A. J. Freeman (see Ref. 37).

TABLE XII. Comparison of Several Hartree-Fock Calculations of $Cl^-$

(Values are in a.u.)

| | | This Calculation Accurate Set | Hartree[a] (Numerical Integration) | Watson and Freeman[b] | This Calculation Simple Set |
|---|---|---|---|---|---|
| $E$ | | -459.57684 | . . . . . | -459.57499 | -459.57362 |
| $\Delta E$ | | 0 | . . . . . | -0.00185 | -0.00322 |
| $\epsilon_{1s}$ | | -104.50546 | $-104.5_5$ | -104.50829 | -104.50086 |
| $\Delta\epsilon_{1s}$ | | 0 | $+0.0_4$ | +0.00283 | -0.00460 |
| $\mathrm{Cusp}_{1s}$ | | -17.0048 | . . . . . | -16.9691 | -16.9635 |
| $\Delta\mathrm{Cusp}_{1s}$ | | +0.0048 | . . . . . | 0.0309 | -0.0365 |
| $\lvert A_o(1s)\rvert$ | | 136.48 | 136.5 | 136.41 | 136.40 |
| $\Delta\lvert A_o(1s)\rvert$ | | 0.0 | 0 | +0.1 | +0.1 |
| $\langle r\rangle_{1s}$ | | 0.09130 | . . . . . | 0.09130 | 0.09130 |
| $\Delta\langle r\rangle_{1s}$ | | 0 | . . . . . | 0.00000 | 0.00000 |
| $\langle r^2\rangle_{1s}$ | | 0.01120 | $0.01_1$ | 0.01120 | 0.01120 |
| $\Delta\langle r^2\rangle_{1s}$ | | 0 | $0.00_0$ | 0.00000 | 0.00000 |
| $[\int(\Delta P_{1s})^2]^{\frac{1}{2}}$ | | 0 | . . . . . | 0.0004 | 0.0005 |
| $\lvert\Delta P_{1s}\rvert_{max}$ | $0 \leq r < \infty$ | 0 | 0.001 | 0.0005 | 0.0008 |
| $\epsilon_{2s}$ | | -10.22916 | $-10.23_5$ | -10.23225 | -10.22595 |
| $\Delta\epsilon_{2s}$ | | 0 | $+0.00_6$ | +0.00309 | -0.00321 |
| $\mathrm{Cusp}_{2s}$ | | -16.9933 | . . . . . | -17.0174 | -16.9902 |
| $\Delta\mathrm{Cusp}_{2s}$ | | -0.0067 | . . . . . | +0.0174 | -0.0098 |
| $\lvert A_o(2s)\rvert$ | | 38.238 | 38.24 | 38.254 | 38.238 |
| $\Delta\lvert A_o(2s)\rvert$ | | 0.00 | 0 | -0.01 | 0.00 |
| $\langle r\rangle_{2s}$ | | 0.44180 | . . . . . | 0.44179 | 0.44181 |
| $\Delta\langle r\rangle_{2s}$ | | 0 | . . . . . | +0.00001 | -0.00001 |
| $\langle r^2\rangle_{2s}$ | | 0.23129 | $0.23_1$ | 0.23129 | 0.23130 |
| $\Delta\langle r^2\rangle_{2s}$ | | 0 | $0.00_0$ | 0.00000 | -0.00001 |
| $[\int(\Delta P_{2s})^2]^{\frac{1}{2}}$ | | 0 | . . . . . | 0.0006 | $\leq$0.0003 |
| $\lvert\Delta P_{2s}\rvert_{max}$ | $0 \leq r < 0.35$ | 0 | 0.001 | 0.0003 | 0.0002 |
| | $0.35 \leq r < \infty$ | 0 | 0.001 | 0.0004 | 0.0003 |
| $\epsilon_{3s}$ | | -0.73320 | -0.727 | -0.73547 | -0.73031 |
| $\Delta\epsilon_{3s}$ | | 0 | -0.006 | +0.00227 | -0.00289 |
| $\mathrm{Cusp}_{3s}$ | | -16.9622 | . . . . . | -17.0158 | -16.7602 |
| $\Delta\mathrm{Cusp}_{3s}$ | | -0.0378 | . . . . . | +0.0158 | -0.2398 |
| $\lvert A_o(3s)\rvert$ | | 11.261 | 11.31 | 11.273 | 11.209 |
| $\Delta\lvert A_o(3s)\rvert$ | | +0.05 | 0 | +0.04 | +0.10 |
| $\langle r\rangle_{3s}$ | | 1.60179 | . . . . . | 1.60163 | 1.60242 |
| $\Delta\langle r\rangle_{3s}$ | | 0 | . . . . . | +0.00016 | -0.00063 |
| $\langle r^2\rangle_{3s}$ | | 3.01041 | $3.01_2$ | 3.01207 | 3.01262 |
| $\Delta\langle r^2\rangle_{3s}$ | | 0 | $-0.00_2$ | -0.00166 | -0.00221 |
| $[\int(\Delta P_{3s})^2]^{\frac{1}{2}}$ | | 0 | . . . . . | 0.0051 | 0.0007 |
| $\lvert\Delta P_{3s}\rvert_{max}$ | $0 \leq r < 1.3$ | 0 | $0.001_5$ | 0.0002 | 0.0010 |
| | $1.3 \leq r < \infty$ | 0 | $0.002_5$ | 0.0032 | 0.0003 |

TABLE XII. Continued

(Values are in a.u.)

| | | This Calculation Accurate Set | Hartree[a] (Numerical Integration) | Watson and Freeman[b] | This Calculation Simple Set |
|---|---|---|---|---|---|
| $\epsilon_{2p}$ | | -7.69557 | $-7.69_5$ | -7.69866 | -7.69225 |
| $\Delta\epsilon_{2p}$ | | 0 | $-0.00_1$ | +0.00309 | -0.00332 |
| $\mathrm{Cusp}_{2p}$ | | -8.4401 | . . . . . | -8.2818 | -8.0692 |
| $\Delta\mathrm{Cusp}_{2p}$ | | -0.0599 | . . . . . | -0.2182 | -0.4308 |
| $\lvert A_0(2p)\rvert$ | | 153.63 | 154.1 | 152.46 | 150.73 |
| $\Delta\lvert A_0(2p)\rvert$ | | +0.5 | 0 | +1.6 | +3.4 |
| $\langle r\rangle_{2p}$ | | 0.40538 | . . . . . | 0.40540 | 0.40525 |
| $\Delta\langle r\rangle_{2p}$ | | 0 | . . . . . | -0.00002 | +0.00013 |
| $\langle r^2\rangle_{2p}$ | | 0.20386 | $0.20_4$ | 0.20387 | 0.20369 |
| $\Delta\langle r^2\rangle_{2p}$ | | 0 | $0.00_0$ | -0.00001 | +0.00017 |
| $[\int(\Delta P_{2p})^2]^{\frac{1}{2}}$ | | 0 | . . . . . | 0.0012 | 0.0034 |
| $\lvert\Delta P_{2p}\rvert_{max}$ | $0 \leq r < \infty$ | 0 | 0.001 | 0.0009 | 0.0031 |
| $\epsilon_{3p}$ | | -0.15017 | $-0.1485_5$ | -0.15172 | -0.14772 |
| $\Delta\epsilon_{3p}$ | | 0 | $-0.0016_2$ | +0.00155 | -0.00245 |
| $\mathrm{Cusp}_{3p}$ | | -8.3803 | . . . . . | -8.6557 | -8.1451 |
| $\Delta\mathrm{Cusp}_{3p}$ | | -0.1197 | . . . . . | +0.1557 | -0.3549 |
| $\lvert A_0(3p)\rvert$ | | 37.927 | 38.02 | 38.601 | 37.468 |
| $\Delta\lvert A_0(3p)\rvert$ | | +0.09 | 0 | -0.58 | +0.55 |
| $\langle r\rangle_{3p}$ | | 2.02880 | . . . . . | 2.03967 | 2.01910 |
| $\Delta\langle r\rangle_{3p}$ | | 0 | . . . . . | -0.01087 | +0.00970 |
| $\langle r^2\rangle_{3p}$ | | 5.10806 | $5.13_7$ | 5.22941 | 5.01079 |
| $\Delta\langle r^2\rangle_{3p}$ | | 0 | $-0.02_9$ | -0.12135 | +0.09727 |
| $[\int(\Delta P_{3p})^2]^{\frac{1}{2}}$ | | 0 | . . . . . | 0.0207 | 0.0209 |
| $\lvert\Delta P_{3p}\rvert_{max}$ | $0 \leq r < 1.5$ | 0 | $0.001_5$ | 0.0028 | 0.0021 |
| | $1.5 \leq r < \infty$ | 0 | $0.001_5$ | 0.0102 | 0.0116 |

[a] D. R. Hartree and W. Hartree (see Ref. 35).

[b] R. E. Watson and A. J. Freeman (see Ref. 37).

Where analytic calculations of other workers are reported, we have used their basis sets to recompute their functions with our program. This was done so that all the properties of each calculation would be available for comparison. Tables IX-XII present the results obtained from our recalculations. Our recalculations agree closely with the original calculations.

The total SCF energies in Tables IX-XII are given to eight significant figures. Although round-off error affects the eighth figure, this is the only way to distinguish the energies of several of the functions. For each orbital, we give the values of the orbital energy $\epsilon_{n\ell}$, cusp, $A_0(n\ell)$, the dominant term in the expansion of the radial-wave function near the origin [defined in Eq. (13)], and the expectation values of $r$ and $r^2$.

Direct comparisons are also made for the radial wave functions $P_{n\ell}(r)$. For each orbital, we give values of the quantity

$$\left[\int_0^\infty [P_{\text{accurate set}}(r) - P_{\text{comparison}}(r)]^2 dr\right]$$

denoted in the tables by $[\int(\Delta P_{n\ell})^2]^{1/2}$. This is a sum of the differences of the radial wave functions over their entire range and may be used as an overall figure of merit for the quality of the comparison function. (This comparison cannot be made with the numerical functions. The radial wave functions obtained with the accurate basis sets and by numerical methods usually agree within one or two units in the last figure given in the tabulation of the numerical functions, and $[\int(\Delta P_{n\ell})^2]^{1/2}$ calculated from these differences would only reflect rounding errors.) The tables also give the maximum value of $|\Delta P(r)| = |P_{\text{accurate set}}(r) - P_{\text{comparison}}(r)|$. For some orbitals, $|\Delta P|_{\max}$ is given for two ranges of r to indicate that the agreement between some of the radial wave functions is considerably better for the inner portion of the function than for the tail. The limit of the ranges is arbitrary. Except for a small range of values of r, usually at the tail of the orbital, $|\Delta P(r)|$ is smaller than $|\Delta P(r)|_{\max}$. Thus $|\Delta P(r)|_{\max}$ gives the worst view of the accuracy of the orbitals.

The differences given in Tables IX-XII ($\Delta E$, $\Delta\epsilon$, etc.) are usually defined as

$$\Delta\text{Property} = \text{Property (accurate set)} - \text{Property (comparison function)}. \tag{14a}$$

The exceptions are

$$\Delta\text{Cusp}_{n\ell} = -Z/(\ell + 1) - \text{Cusp}_{n\ell}\ \text{(comparison function)}, \tag{14b}$$

and

$$\Delta |A_0(n\ell)| = |A_0(n\ell)\ [\text{numerical calculation}]| - |A_0(n\ell)\ [\text{comparison function}]|. \tag{14c}$$

For $A_0(n\ell)$, numerical calculations were chosen as a standard of comparison because numerical techniques require that the radial functions be determined accurately at the origin. The numerical integration is started outward from $r = 0$, and the results are sensitive to any error in the function at the origin.

The values of the radial wave functions obtained from the accurate basis SCF calculations agree strikingly well with the values obtained from numerical calculations.

Worsley$^{(32)}$ gives the neon radial functions, tabulated at logarithmic intervals, to four decimal places except for the tail region of each orbital where they are given to only three decimal places. Worsley claims that the functions are accurate to within two or three units in the last figure given. At every point Worsley tabulates, the difference between our accurate set results and her numerical results, $|\Delta P(r)|$, is within this limit except for four points. At the great majority of tabulated points, $|\Delta P(r)|$ is 0 or 1 in the last figure Worsley gives.

Froese$^{(33)}$ claims that her radial wave functions for $F^-$, given to four decimal places, are accurate to 0.0002. The differences with our accurate-set results are within this limit with only a few exceptions. At two points, $|\Delta P_{1s}(r)| = 0.0003$; at ten points, $|\Delta P_{2s}(r)|$ is between 0.0003 and 0.0005; and at five points, $|\Delta P_{2p}(r)|$ is between 0.0003 and 0.0005.

Hartree and Hartree$^{(34,35)}$ give the radial wave functions for Ar and $Cl^-$ to three decimal places; for the 3s and 3p orbitals of $Cl^-$, they tabulate $2P(r)$ rather than $P(r)$ in order to obtain additional accuracy. For argon, $|\Delta P_{1s}(r)|$ has its largest values at five consecutive points and is between 0.003 and 0.007; at several points of the 2s and 2p radial functions, $|\Delta P(r)|$ has its maximum value of 0.002. For the argon 3s and 3p radial functions, $|\Delta P(r)|$ is usually 0.000 and is never larger than 0.001 (i.e., 0 or 1 in the last figure that Hartree and Hartree give). The relatively large disagreements for the 1s, 2s, and 2p radial functions occur because Hartree and Hartree did not obtain these functions by direct solution of the HF integro-differential equations but rather by an interpolation between results for $Cl^-$ and $K^+$. Their 3s and 3p functions, on the other hand, were obtained as self-consistent numerical solutions of the HF equations. This explanation is supported by the fact that, for the 1s, 2s, and 2p orbitals of the Hartree and Hartree calculation on $Cl^-$, $|\Delta P(r)|$ is never larger than 0.001. Although the agreement between our results and those of Hartree and Hartree for the 3s and 3p orbitals of $Cl^-$ is still good, it is not as good for these orbitals as for the others. For the 3s radial function, $2\|\Delta P(r)\|$ is 0.005 at one point in the tail of the function, 0.004 at the two adjacent points, and 0.002 or 0.003 at several points; for the 3p function, there are also several points for which $2|\Delta P(r)|$ is as large as 0.002 and 0.003.

For Ne, $F^-$, Ar, and $Cl^-$, the agreement between the numerical and accurate basis set analytic radial functions is, in almost all cases, within the error of the numerical calculations. The 3s and 3p radial functions of $Cl^-$ obtained by Hartree and Hartree are slightly more accurate than the accurate basis set analytic functions.

The differences between the orbital energies $\epsilon_{n\ell}$ obtained from the accurate set analytic SCF calculations and from the numerical calculations are sometimes larger than might be expected from the small differences between the radial wave functions. This can be explained from the different way that the $\epsilon$'s are obtained by the two methods. In the analytic method, the $\epsilon$ given is obtained directly as the expectation value of the Fock operator for the orbital, $\epsilon_{n\ell} = \langle \phi_{n\ell}|F|\phi_{n\ell}\rangle$. In the numerical calculations discussed, $\epsilon$ is treated simply as a parameter to be adjusted until the solutions of the HF equations approximately satisfy the boundary conditions placed on them. The results of the accurate analytic SCF calculations should give better values of the $\epsilon$'s than the numerical calculations.

The accuracy of the accurate basis set SCF functions given in Tables I-IV has been estimated. The estimates used the techniques described above and, in large part, the information given in Tables IX-XII. The estimates are generous and probably indicate, for most of the functions, errors larger than the true errors.

The total SCF energy, $E_{SCF}$, represents the exact HF total energy to within two units in the seventh significant figure, and the $\epsilon_{n\ell}$'s are accurate to about five units in the same decimal place that the error enters the total energy. When $E_{SCF} < 100$, the $\epsilon_{n\ell}$'s are accurate to five units in the fifth decimal place, and when $E_{SCF} \geq 100$, to five units in the fourth decimal place.

For the states of the heavier atoms (chlorine, argon, and potassium) the 1s, 2s, and 2p radial wave functions do not differ from the exact HF solutions, for any value of r, by more than 0.0005. The 1s radial function is probably accurate to within 0.0002. The 3s and 3p radial functions are definitely accurate to within 0.0015, and over much of the range of r are accurate to within 0.0005. The only exception is the 3s radial function of $Cl^-$, where 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 (fluorine, neon, and sodium), the radial functions are accurate to within 0.0005. The 1s radial function is accurate to within 0.0002. The 2s and 2p radial functions have an error smaller than 0.0005.

The radial wave function of the outermost s shell (2s for the light atoms, and 3s for the heavier atoms) is the least accurate function for any 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 optimize the total energy.

The accurate set SCF functions given in Tables I-IV, except for $Cl^-$ and the 1s-hole state of $K^+$, represent the limit of accuracy which can be obtained using the single-precision, eight-significant-figure, floating-point arithmetic of the IBM 704 and 7094 computers. The $Cl^-$ SCF function could probably be improved with the addition to the basis set of an s, and possibly a p, basis function. The function for the 1s-hole state of $K^+$ could be improved slightly if the numerical evaluation in the exponent variation procedures were altered to minimize round-off error. (This change has already been made in the latest versions of the SCF programs.)

C. Properties of the SCF Wave Functions

Expectation values of r and $r^2$, for all the states computed are given in Tables XIII and XIV. These expectation values were calculated from the accurate basis set SCF functions. For each state, the expectation values of r and $r^2$ given are taken with respect to each occupied orbital, $\langle r\rangle_{n\ell} = \int_0^\infty [P_{n\ell}(r)]^2 r\,dr$ and $\langle r^2\rangle_{n\ell} = \int_0^\infty [P_{n\ell}(r)]^2 r^2 dr$. In addition, the average values of the $\langle r\rangle$ and $\langle r^2\rangle$ are given. The average value of $\langle r\rangle$ is defined by $\Sigma N_{n\ell}\langle r\rangle_{n\ell}/\Sigma N_{n\ell}$, where $N_{n\ell}$ is the electron occupation of the $n\ell^{th}$ orbital and the sum is over all occupied orbitals. The values of $\langle r\rangle_{n\ell}$ and $\langle r^2\rangle_{n\ell}$ represent the exact HF values to within a few units in the last figure given. The values of $\langle r^2\rangle_{n\ell}$ for the outermost s and p orbitals of a system are least accurate, and the errors may be as large as 20 units in the last figure. These estimates of accuracy may be checked by reference to the comparisons given in Tables IX-XII.

An extra figure is given for the average values of $\langle r\rangle$ and $\langle r^2\rangle$ to avoid round-off error if these values are multiplied by the total number of electrons in the system to give $\langle\Sigma r_i\rangle$ and $\langle\Sigma r_i^2\rangle$.

Nonzero overlap integrals between many-electron SCF wave functions, calculated from the accurate basis set SCF functions, are given in Table XV. These results are presented in connection with the discussion, at the end of Section II, of the lack of orthogonality between excited- and ground-state SCF functions of the same symmetry.

TABLE XIII. Expectation Values of r and $r^2$ for $F^-$, Ne, and $Na^+$ and $n\ell$-hole States of $F^-$, Ne, and $Na^+$

(Values are in a.u.; 1 Bohr = 0.52917A)

| | $F^-(^1S)$ | $F(^2P)$<br>2p-hole | $F(^2S)$<br>2s-hole | $F(^2S)$<br>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 |
| $\Sigma N_i\langle r\rangle_i/\Sigma N_i$ | 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 |
| $\Sigma N_i\langle r^2\rangle_i/\Sigma N_i$ | 1.59783 | 1.13672 | 1.18988 | 1.06166 |
| | $Ne(^1S)$ | $Ne^+(^2P)$<br>2p-hole | $Ne^+(^2S)$<br>2s-hole | $Ne^+(^2S)$<br>1s-hole |
| $\langle r\rangle_{1s}$ | 0.1576 | 0.1576 | 0.1578 | 0.1454 |
| $\langle r\rangle_{2s}$ | 0.8921 | 0.8603 | 0.8536 | 0.8171 |
| $\langle r\rangle_{2p}$ | 0.9652 | 0.8759 | 0.8841 | 0.7993 |
| $\Sigma N_i\langle r\rangle_i/\Sigma N_i$ | 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 |
| $\Sigma N_i\langle r^2\rangle_i/\Sigma N_i$ | 0.93682 | 0.75081 | 0.77351 | 0.72903 |
| | $Na^+(^1S)$ | $Na^{++}(^2P)$<br>2p-hole | $Na^{++}(^2S)$<br>2s-hole | $Na^{++}(^2S)$<br>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 |
| $\Sigma N_i\langle r\rangle_i/\Sigma N_i$ | 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 |
| $\Sigma N_i\langle r^2\rangle_i/\Sigma N_i$ | 0.64130 | 0.53945 | 0.54949 | 0.53645 |

TABLE XIV. Expectation Values of r and $r^2$ for $Cl^-$, Ar, and $K^+$ and $n\ell$-hole States of $Cl^-$, Ar, and $K^+$

(Values are in a.u.; 1 Bohr = 0.52917A)

| | $Cl^-(^1S)$ | $Cl(^2P)$ 3p-hole | $Cl(^2S)$ 3s-hole | $Cl(^2P)$ 2p-hole | $Cl(^2S)$ 2s-hole | $Cl(^2S)$ 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 |
| $\Sigma N_i\langle r\rangle_i/\Sigma N_i$ | 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 |
| $\Sigma N_i\langle r^2\rangle_i/\Sigma N_i$ | 2.13207 | 1.62498 | 1.68842 | 1.59608 | 1.59830 | 1.54220 |

| | $Ar(^1S)$ | $Ar^+(^2P)$ 3p-hole | $Ar^+(^2S)$ 3s-hole | $Ar^+(^2P)$ 2p-hole | $Ar^+(^2S)$ 2s-hole | $Ar^+(^2S)$ 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 |
| $\Sigma N_i\langle r\rangle_i/\Sigma N_i$ | 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 |
| $\Sigma N_i\langle r^2\rangle_i/\Sigma N_i$ | 1.44565 | 1.18672 | 1.22406 | 1.19586 | 1.19821 | 1.15911 |

| | $K^+(^1S)$ | $K^{++}(^2P)$ 3p-hole | $K^{++}(^2S)$ 3s-hole | $K^{++}(^2P)$ 2p-hole | $K^{++}(^2S)$ 2s-hole | $K^{++}(^2S)$ 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 |
| $\Sigma N_i\langle r\rangle_i/\Sigma N_i$ | 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 |
| $\Sigma N_i\langle r^2\rangle_i/\Sigma N_i$ | 1.08532 | 0.92071 | 0.94407 | 0.94193 | 0.94416 | 0.91592 |

TABLE XV. Overlap Integrals between Total SCF Wave Functions of the $n\ell$-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 |

## D. Validity of the Exponent Variation Procedure for Excited States

The basis-function exponent variation procedure, described in Section III, selects values of the exponents that minimize the total SCF energy. This is a valid procedure for ground states and excited states that are the lowest states of a symmetry species. SCF functions for these states give stationary values of the energy that are absolute minima. It is not known whether the SCF functions for the higher excited states of a symmetry species give stationary values of the energy that are relative minima or some other sort of extrema. The problem, for these excited states, is that exponents chosen to minimize the total energy may not give SCF functions that are optimum representations of the true HF solutions.

If explicit variational equations, e.g., those given by Dehn,(26) were solved for the exponents of the basis functions, there would be no difficulty with the higher excited states. In this way, stationary values of the energy would be found with respect to variation of the exponents as well as the linear coefficients, $C_{n\ell,p}$. However, when our exponent variation procedure is used, a particular stationary value of the energy with respect to variation of the exponents is found in a brute-force fashion. This point was discussed in Section III. The particular stationary value found is a minimum. For all the exponent variations performed to obtain the SCF functions reported in this paper, this stationary value was found with no more difficulty for the excited states than for the ground states.

It seems unlikely, for an analytic-expansion SCF function of a particular state, that there will be more than one stationary value of the energy. It is reasonable that the solutions of variational equations for both the $C_{n\ell,p}$'s and the exponents are unique. If this is true, then the use of our exponent variation procedure is justified.

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. This can be easily confirmed by reference to Tables I-VIII. Further, as may be seen from Table XVIII, the calculated ionization potentials, for the removal of inner-shell electrons, agree quite well with experimental values.

The success of our method of exponent variation implies that the total energy of analytic-expansion SCF functions, even for excited states, is an upper bound to the exact HF energy. The results in Table XVIII also show quite clearly that the SCF energies are, in fact, upper bounds to the exact, nonrelativistic, total energies. According to estimates made by Clementi,(43) the exact nonrelativistic energy is ~0.4 Hartree below the SCF energy for $F^-$, Ne, and $Na^+$ ($E_{nr} = E_{SCF} - 0.4$) and ~0.7 Hartree below the SCF energy for $Cl^-$, Ar, and $K^+$ ($E_{nr} = E_{SCF} - 0.7$). The calculated ionization potential $IP(\Delta E_{SCF})$ is obtained by subtracting the SCF energy of the parent from that of the ion; i.e., $IP(\Delta E_{SCF}) = E_{SCF}(\text{ion}) - E_{SCF}(\text{parent})$. Suppose the SCF energies of the inner-shell hole states were not upper bounds to the exact energies. Then $IP(\Delta ESCF)$ for the removal of an inner-shell electron would have to be much smaller than the true nonrelativistic ionization potential; at least 0.4 smaller for the neon-like ions and 0.7 smaller for the argon-like ions. This is obviously not the case.

## E. Effect of the Off-diagonal Lagrangian Multipliers

The constraint, given in Eq. (7), that the SCF orbitals belonging to the same symmetry species be orthogonal is incorporated by introducing off-diagonal Lagrangian multipliers into the HF equations.(2-5) Orbitals of different symmetry are, of course, automatically orthogonal. For closed-shell systems, a unitary transformation can be found between the occupied orbitals that puts the matrix of Lagrangian multipliers into diagonal form. This additional requirement that the off-diagonal Lagrangian multipliers be zero serves, in fact, to uniquely define the SCF orbitals. For open-shell systems, it is possible to find a unitary transformation between the closed-shell orbitals for which the off-diagonal Lagrangian multipliers coupling the closed shells are zero. However, the Lagrangian multipliers that couple open and closed shells of the same symmetry cannot be reduced to zero.(3,4)

In other treatments, the nonzero off-diagonal Lagrangian multipliers are introduced into the HF equations as inhomogeneous terms;(16,29) i.e.,

$$F\phi_i = \epsilon_i\phi_i + \Sigma_{j\neq i}\theta_{ji}\phi_j. \qquad (15)$$

Because of the difficulty of handling these additional inhomogeneous terms, the off-diagonal Lagrangian multipliers are often treated in an approximate way.(13,14,42) Roothaan(3,4) 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 preserving the pseudoeigenvalue form of the HF equations.

This method is especially suitable for the matrix form of the HF equations. The matrix HF operators(4) are

$$\underset{\sim}{F}_{C\ell} = \underset{\sim}{H}_{\ell} + \underset{\sim}{P}_{\ell} + \underset{\sim}{R}_{O\ell},$$

and (16)

$$\underset{\sim}{F}_{O\ell} = \underset{\sim}{H}_{\ell} + \underset{\sim}{P}_{\ell} - \underset{\sim}{Q}_{\ell} + \underset{\sim}{R}_{C\ell};$$

where $\underset{\sim}{F}_{C\ell}$ and $\underset{\sim}{F}_{O\ell}$ are closed-shell and open-shell Fock operators, respectively, for symmetry species $\ell$, $\underset{\sim}{H}_{\ell}$ is the one-electron operator, $\underset{\sim}{P}_{\ell}$ and $\underset{\sim}{Q}_{\ell}$ are combinations of Coulomb and exchange operators, and $\underset{\sim}{R}_{O\ell}$ and $\underset{\sim}{R}_{C\ell}$ are the coupling operators. (The eigenvalue problem is $\underset{\sim}{F}\underset{\sim}{c} = \epsilon \underset{\sim}{S}\underset{\sim}{c}$ where $\underset{\sim}{S}$ is the overlap matrix.) Let the index k stand only for closed-shell orbitals, and m only for open-shell orbitals; the coupling operators are defined so that for self-consistent eigenvectors of $\underset{\sim}{F}_{C\ell}$ and $\underset{\sim}{F}_{O\ell}$,

$$\underset{\sim}{R}_{O\ell}\underset{\sim}{c}_{k\ell} = \Sigma(-\theta_{m\ell,k\ell}\underset{\sim}{c}_{m\ell}),$$

and (17)

$$\underset{\sim}{R}_{C\ell}\underset{\sim}{c}_{m\ell} = \Sigma(-\theta_{k\ell,m\ell}\underset{\sim}{c}_{k\ell}).$$

The $\theta_{m\ell,k\ell}$ and $\theta_{k\ell,m\ell}$ are the off-diagonal Lagrangian multipliers that couple the open and closed shells; Note that they are not symmetric, but that

$$N_{O\ell}\theta_{k\ell,m\ell} = N_{C\ell}\theta_{m\ell,k\ell}, \qquad (18)$$

where $N_{C\ell}$ and $N_{O\ell}$ are the electron occupations of the closed shells and open shell, respectively, of symmetry $\ell$.

The values of the nonzero off-diagonal Lagrangian multipliers for the $n\ell$-hole states of argon and neon are given in Table XVI. These values were computed with the accurate set SCF functions reported in Tables I-IV. 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 $n\ell$-hole states of $Cl^-$ and $K^+$, and $F^-$ and $Na^+$ are similar to the values given in Table XVI for argon and neon.

TABLE XVI. Off-diagonal Lagrangian Multipliers for the $n\ell$-hole States of Argon and Neon*

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

*The Lagrangian multipliers are not symmetric; $\theta_{\text{closed, open}} = (N_c/N_o)\,\theta_{\text{open, closed}}$, where $N_c$ and $N_o$ are the electron occupations of the closed and open shells, respectively.

The most striking effect of the inclusion of the off-diagonal Lagrangian multipliers is that the 1s orbitals, of the 1s-hole states of $Cl^-$, Ar, and $K^+$, <u>have a node</u>. In each of these cases, $P_{1s}(r)$ goes through zero and reaches a minimum value of -0.003. For example, $P_{1s}(r)$ for $Ar^+$ (1s-hole) is zero for $r = 0.93$ Bohr and has a minimum of -0.0028 for $1.30 \leq r \leq 1.45$. For large r, the HF equation for $P_{1s}(r)$ becomes

$$\epsilon_{1s}P_{1s}(r) \cong -\theta_{2s,1s}P_{2s}(r) - \theta_{3s,1s}P_{3s}(r). \qquad (19)$$

For $Ar^+$ (1s-hole), when the values in Tables III and XVI are used, Eq. (19) becomes

$$P_{1s}(r) \cong +0.01142P_{2s}(r) - 0.00357P_{3s}(r), \qquad (20)$$

and the second term is dominant since the 2s radial function goes to zero much before the 3s radial function does. For $r \geq 1.2$ Bohrs, $P_{1s}(r)$ calculated from Eq. (20), using the accurate-set 2s and 3s radial functions, agrees with the accurate-set analytic SCF 1s radial function to within

0.00006. The error is always less than 3%; this is remarkably good agreement, especially since the analytic expansion method does not give exact solutions of the integro-differential HF equations.

The dominant terms, in the HF equations, that determine the behavior of inner-shell orbitals at large r are the nonzero off-diagonal Lagrangian multipliers with the outer-shell orbitals. 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, for the states reported in this paper, are positive. The effect of the positive off-diagonal Lagrangian multipliers is to extend the tails of the orbitals rather than to introduce additional nodes.

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 $r \rightarrow 0$. Because of this choice, the values of $P_{n\ell}(r)$ in the $(n - \ell)^{th}$ loop, usually the outermost loop of the orbital, will be positive. This is a departure from the convention usually used in numerical HF calculations,(16,32-35) which is that all radial functions are positive as $r \rightarrow 0$.

The negative value of $\theta_{3s,1s}$ should 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.

To get further insight into the importance of the off-diagonal Lagrangian multipliers, an approximate treatment was developed. The matrices $\underset{\sim}{R}_{O\ell}$ and $\underset{\sim}{R}_{C\ell}$ were arbitrarily set equal to zero, and "self-consistent" solutions using the operators,

$$\underset{\sim}{F}'_{C\ell} = \underset{\sim}{H}_{\ell} + \underset{\sim}{P}_{\ell}$$

and (21)

$$\underset{\sim}{F}'_{O\ell} = \underset{\sim}{H}_{\ell} + \underset{\sim}{P}_{\ell} - \underset{\sim}{Q}_{\ell},$$

rather than $\underset{\sim}{F}_{C\ell}$ and $\underset{\sim}{F}_{O\ell}$ of Eq. (16), were obtained. The occupied open-shell eigenvector of $\underset{\sim}{F}'_{O\ell}$ is not orthogonal to the occupied closed-shell eigenvectors of $\underset{\sim}{F}'_{O\ell}$. Since the operators of Eqs. (16) and (21) are assumed to be constructed from an orthogonal set of orbitals, the open-shell eigenvector was Schmidt-orthogonalized to the closed-shell eigenvectors. This Schmidt orthogonalization does not change the total determinantal wave function. A "self-consistent" solution was obtained when the Schmidt-orthogonalized eigenvectors of $\underset{\sim}{F}'_{O\ell}$ and $\underset{\sim}{F}'_{C\ell}$ were the same, within convergence thresholds, as the orthogonal vectors used to construct the operators $\underset{\sim}{F}'_{O\ell}$ and $\underset{\sim}{F}'_{C\ell}$ of Eq. (21).

Since this method neglects the off-diagonal Lagrangian multipliers in constructing the operators $\underset{\sim}{F}'_{O\ell}$ and $\underset{\sim}{F}'_{C\ell}$, "self-consistent" solutions obtained, using $\underset{\sim}{F}'_{O\ell}$ and $\underset{\sim}{F}'_{C\ell}$, are denoted by NLM (Neglect Lagrangian Multipliers) to distinguish them from the SCF solutions obtained using the operators of Eq. (16).

NLM calculations were performed, using the accurate basis sets of Tables I and III, for the $n\ell$-hole states of argon and neon. The results of these calculations are given in Table XVII. 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 XVII differ slightly, because of round-off, from the values given in Tables I-IV. Values of the total energy E (in Hartrees), V/T, and the overlap integrals $S_{n\ell,n'\ell}$ between the occupied eigenvector of $\underset{\sim}{F}'_{O\ell}$ and the occupied eigenvectors of $\underset{\sim}{F}'_{C\ell}$ are given. The signs of the $S_{n\ell,n'\ell}$ are determined by the sign conventions stated above for the SCF orbitals.

The NLM results for states with outer-shell vacancies are almost the same as the SCF results, and the $S_{n\ell,n'\ell}$ are quite small. However, for the states with inner-shell vacancies, where the off-diagonal Lagrangian multipliers are large, the NLM results are quite different from the SCF results, and the $S_{n\ell,n'\ell}$ are large.

## F. Comparison of SCF Ionization Potentials with Experiment

Experimental data are available for most of the ionization potentials (IP's) of the closed-shell systems of $F^-$, Ne, $Na^+$, $Cl^-$, Ar, and $K^+$. This includes the IP's for the removal of an electron from any occupied shell. A comparison with experiment of IP's calculated from the SCF wave functions is presented in Table XVIII. The IP for the removal of an outer-shell electron (3s or 3p shell of the argon-like ions, and 2s or 2p shell of the neon-like ions) can usually be determined from Moore's optical data.(31) The electron affinities of $F^-$ and $Cl^-$ (i.e., the 2p-hole IP of $F^-$, and the 3p-hole IP of $Cl^-$) have been determined very accurately by Berry, Reimann, and Spokes.(43,44) The only state for which experimental data do not seem to be available is the 3s-hole state of $Cl^-$; but Varsavsky(45) reports an estimate made by Rohrlich of the term value of this state.

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 example, for the argon-like ions, the IP for the removal of a 1s electron is

TABLE XVII. Effect of Neglecting the Off-diagonal Lagrangian Multipliers for the nℓ-hole States of Argon and Neon (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)* | E(NLM)<br>[E(SCF)-E(NLM)] | V/T(SCF)* | 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<br>[0.0000] | -1.999999 | -1.999972 | 3s | $-0.0000_1$ | $+0.0009_3$ | .... |
| $Ar^+$(2s-hole) | -514.8794 | -514.8808<br>[+0.0014] | -2.000000 | -2.000242 | 2s | $+0.0003_9$ | .... | $-0.0104_4$ |
| $Ar^+$(1s-hole) | -409.3890 | -409.3941<br>[+0.0051] | -2.000000 | -2.001786 | 1s | .... | $-0.0062_2$ | $+0.0017_6$ |
| | | | | | | $S_{np,1p}$ | $S_{np,2p}$ | |
| $Ar^+$(3p-hole) | -526.2744 | -526.2744<br>[0.0000] | -1.999999 | -1.999966 | 3p | $+0.0003_5$ | .... | |
| $Ar^+$(2p-hole) | -517.6690 | -517.6746<br>[+0.0056] | -2.000000 | -2.000464 | 2p | .... | $-0.0043_8$ | |
| | | | | | | $S_{ns,1s}$ | $S_{ns,2s}$ | |
| $Ne^+$(2s-hole) | -126.7348 | -126.7348<br>[0.0000] | -2.000003 | -1.999897 | 2s | $+0.0005_3$ | .... | |
| $Ne^+$(1s-hole) | -96.62571 | -96.62983<br>[+0.00412] | -1.999997 | -2.003008 | 1s | .... | $-0.0102_2$ | |

*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 I and III, which are from calculations performed on the IBM 7094.

TABLE XVIII. Comparison of SCF and Experimental Ionization Potentials for the $n\ell$-hole States of $F^-$, Ne, $Na^+$, $Cl^-$, Ar, and $K^+$
(energies are in Hartree; 1 Hartree = 27.2098 eV = 2.194746 x $10^5$ $cm^{-1}$)

| State | | | IP(exp)[a] | IP(nr)[a] | $IP(-\varepsilon_{n\ell})$ | IP(exp)[b] - $IP(-\varepsilon_{n\ell})$ | $IP(\Delta E_{SCF})$ | IP(exp)[b] - $IP(\Delta E_{SCF})$ |
|---|---|---|---|---|---|---|---|---|
| | $F^-$[c,d] | | 0.1273 | . . . . | 0.1810 | -0.0537<br>(-1.461 eV) | 0.0501 | +0.0772<br>(+2.101 eV) |
| 2p-hole $1s^22s^2\underline{2p}^5$ | Ne[d] | | 0.7937 | . . . . | 0.8503 | -0.0566<br>(-1.540 eV) | 0.7293 | +0.0644<br>(+1.752 eV) |
| | $Na^+$[d] | | 1.7404 | . . . . | 1.7972 | -0.0568<br>(-1.546 eV) | 1.6796 | +0.0608<br>(+1.654 eV) |
| | $F^-$[c,d] | | 0.8947 | . . . . | 1.0746 | -0.1799<br>(-4.895 eV) | 0.9282 | -0.0335<br>(-0.912 eV) |
| 2s-hole $1s^2\underline{2s}2p^6$ | Ne[d] | | 1.7814 | . . . . | 1.9303 | -0.1489<br>(-4.052 eV) | 1.8123 | -0.0309<br>(-0.841 eV) |
| | $Na^+$[d] | | 2.9433 | . . . . | 3.0737 | -0.1304<br>(-3.548 eV) | 2.9682 | -0.0249<br>(-0.678 eV) |
| | $F^-$[e] | | $24.99_1$[f] | $24.96_7$ | 25.8296 | $-0.86_3$<br>($-23.4_8$ eV) | 24.9353 | $+0.03_2$<br>($+0.8_7$ eV) |
| 1s-hole $\underline{1s}2s^22p^6$ | Ne[e] | | 31.970[f]<br>31.984[g] | $31.94_5$[g] | 32.7723 | $-0.82_7$<br>($-22.5_0$ eV) | 31.9214 | $+0.02_4$<br>($+0.6_5$ eV) |
| | $Na^+$[e] | | $39.99_9$[f] | $39.93_8$ | 40.7597 | $-0.82_2$<br>($-22.3_7$ eV) | 39.9345 | $+0.00_3$<br>($+0.0_8$ eV) |
| | $Cl^-$[c,d] | | 0.1341 | . . . . | 0.1502 | -0.0161<br>(-0.438 eV) | 0.0948 | +0.0393<br>(+1.069 eV) |
| 3p-hole $1s^22s^22p^63s^2\underline{3p}^5$ | Ar[d] | | 0.5813 | . . . . | 0.5909 | -0.0096<br>(-0.261 eV) | 0.5430 | +0.0383<br>(+1.042 eV) |
| | $K^+$[d] | | 1.1726 | . . . . | 1.1705 | +0.0021<br>(+0.057 eV) | 1.1260 | +0.0466<br>(+1.268 eV) |
| | $Cl^-$[c,h] | | $0.52_6$(?) | . . . . | 0.7332 | $-0.20_7$<br>($-5.6_3$ eV) | 0.6601 | $-0.13_4$<br>(-3.65 eV) |
| 3s-hole $1s^22s^22p^6\underline{3s}3p^6$ | Ar[d] | | 1.0745 | . . . . | 1.2773 | -0.2028<br>(-5.518 eV) | 1.2198 | -0.1453<br>(-3.954 eV) |
| | $K^+$[d] | | 1.7644 | . . . . | 1.9638 | -0.1994<br>(-5.426 eV) | 1.9136 | -0.1492<br>(-4.060 eV) |
| | Cl[e] | $^2P_{3/2}$ | $7.22_0$[i]<br>$7.24_2$(?)[j] | $7.22_8$[i] | 7.6956 | $-0.46_8$<br>($-12.7_3$ eV) | 7.2420 | $-0.01_4$<br>( $0.3_8$ eV) |
| | | $^2P_{1/2}$ | $7.21_9$[i]<br>$7.30_1$(?)[j] | | | | | |
| 2p-hole $1s^22s^2\underline{2p}^53s^23p^6$ | Ar[3] | $^2P_{3/2}$ | $9.13_3$[i]<br>$9.1_1$[j] | $9.14_2$[i] | 9.5713 | $-0.42_9$<br>($-11.6_7$ eV) | 9.1484 | $-0.00_6$<br>($-0._2$ eV) |
| | | $^2P_{1/2}$ | $9.20_9$[i]<br>$9.2_0$[j] | | | | | |
| | $K^+$[e] | $^2P_{3/2}$ | $11.30_6$[i]<br>$11.30_8$[j] | $11.31_5$[i] | 11.7381 | $-0.42_3$<br>($-11.5_1$ eV) | 11.3342 | $-0.01_9$<br>($-0.5_2$ eV) |
| | | $^2P_{1/2}$ | $11.41_6$[i]<br>$11.41_1$[j] | | | | | |
| | $Cl^-$[k] | | $9.7_3$(?) | . . . . | 10.2292 | . . . . | 9.8114 | . . . . |
| 2s-hole $1s^2\underline{2s}2p^63s^23p^6$ | Ar | | . . . . | . . . . | 12.3219 | . . . . | 11.9380 | . . . . |
| | $K^+$[k] | | $14.4_1$(?) | . . . . | 14.7080 | . . . . | 14.3455 | . . . . |
| | $Cl^-$[e] | | $103.59_7$[l]<br>$103.61_9$(?)[m,n] | $103.1_8$[l] | 104.5055 | $-1.3_3$<br>($-36._2$ eV) | 103.2947 | $-0.1_1$<br>($-3._0$ eV) |
| 1s-hole $\underline{1s}2s^22p^63s^23p^6$ | Ar[e] | | $117.83_4$[l]<br>$117.83_5$[g] | $117.3_0$ | 118.6101 | $-1.3_1$<br>($-35._6$ eV) | 117.4284 | $-0.1_3$<br>($-3._5$ eV) |
| | $K^+$[e] | | $113.09_3$[l]<br>$133.09_5$[m]<br>$133.08_8$[n] | $132.4_2$ | 133.7521 | $-1.3_3$<br>($-36._2$ eV) | 132.5890 | $-0.1_7$<br>($-4._6$ eV) |

[a] IP(exp) is the experimental value of the ionization potential. For $^2P$ terms, unless explicitly indicated otherwise, the IP is given to the center of gravity of the term. IP(exp) does not include any correction for the finite mass of the nucleus. IP(nr) is the experimental ionization potential corrected for relativistic effects and the finite mass of the nucleus. The relativistic corrections are made with data taken from Pekeris (Ref. 46) and Scherr et al. (Ref. 47). For discussion of the relativistic corrections, see the text.

[b] SCF values are compared with IP(exp) unless a value of IP(nr) is given; in the latter case, comparisons are made with IP(nr).

[c] Experimental data for the electron affinity of $F^-$ and $Cl^-$ are from Berry and Reimann (Ref. 43).

[d] Experimental data are from Vol. I by Moore (Ref. 31) and correction for $^2P$ separation of the 3p-hole state of $Cl^-$ in Vol. III.

[e] Ionization potentials are obtained by combining the ionization potentials for the outer-shell vacancy states with experimental data on X-ray emission lines. For the 1s-hole states of argon and neon, measurements of the K absorption edge are also used. For sources of X-ray data, see text.

[f] Experimental ionization potential are obtained from the relation IP(1s-hole) = $\Delta E(K\alpha_1)$ + IP(2s-hole; $^2P_{3/2}$).

[g] K absorption edge is as measured by Brogren (Ref. 49).

[h] Estimate of the 3s-hole term value is given by Varsavsky (Ref. 45).

[i] Experimental ionization potential is obtained from the relation IP(2p-hole; $^2P_{3/2,1/2}$) = $-\Delta E(K\alpha_{1,2})$ + $\Delta E(K\beta_1)$ + IP(3p-hole; $^2P_{3/2}$).

[j] Experimental ionization potential is obtained from the relation IP(2p-hole; $^2P_{3/2,1/2}$) = $\Delta E(L\ell,\eta)$ + IP(3s-hole).

[k] The experimental ionization potential is obtained from a table of normal energy levels of atoms; Table 13146 of Landolt-Börnstein (Ref. 48). A correction is added to account for the fact that the zero of energy of a free atom is not the same as that used in the Landolt-Börnstein table. The correction for $K^+$ is +0.56 Hartree, and for $Cl^-$ is -0.17 Hartree.

[l] Experimental ionization potential is obtained from the relation IP(1s-hole) = $\Delta E(K\beta_1)$ + IP(3p-hole; $^2P_{3/2}$).

[m] Experimental ionization potential is obtained from the relation IP(1s-hole) = $\Delta E(K\alpha_1)$ + $\Delta E(L\ell)$ + IP(3s-hole).

[n] Experimental ionization potential is obtained from the relation IP(1s-hole) = $\Delta E(K\alpha_2)$ + $\Delta E(L\eta)$ + IP(3s-hole).

$$\begin{aligned} \mathrm{IP}(1s\text{-hole},\ {}^2S_{1/2}) &= \mathrm{IP}(3p\text{-hole},\ {}^2P_{3/2}) + \Delta E(K\beta_1) \\ &= \mathrm{IP}(3s\text{-hole},\ {}^2S_{1/2}) + \Delta E(L\ell) + \Delta E(K\alpha_1) \\ &= \mathrm{IP}(3s\text{-hole},\ {}^2S_{1/2}) + \Delta E(L\eta) + \Delta E(K\alpha_2), \end{aligned} \tag{22}$$

where the configuration and level of the final state of the ion are given in parentheses after IP, and $\Delta E(K\beta_1)$, $\Delta E(K\alpha_1)$, etc., are the energies of the X-ray emission lines $K\beta_1$, $K\alpha_1$, etc., respectively. Standard X-ray notation is used to describe the emission lines; $K\beta_1$, $K\alpha_1$, and $K\alpha_2$ denote the transitions 1s-hole, ${}^2S_{1/2} \rightarrow$ 3p-hole, ${}^2P_{3/2}$ ($KM_{III}$), 1s-hole, ${}^2S_{1/2} \rightarrow$ 2p-hole, ${}^2P_{3/2}(KL_{III})$, and 1s-hole, ${}^2S_{1/2} \rightarrow$ 2p-hole, ${}^2P_{1/2}(KL_{II})$, respectively; and $L\ell$ and $L\eta$ denote the transitions 2p-hole, ${}^2P_{3/2} \rightarrow$ 3s-hole, ${}^2S_{1/2}(L_{III}M_I)$ and 2p-hole, ${}^2P_{1/2} \rightarrow$ 3s-hole, ${}^2S_{1/2}(L_{II}M_I)$, respectively. For the 1s-hole IP of neon and argon, the K absorption limits ($1s \rightarrow \infty$) of gaseous neon and argon, determined by Brogren,(49) may also be used. (We have used absorption limit here in the same sense as series limit is used for optical spectra; that is, the removal of the electron to infinity with zero kinetic energy.)

Except for the inert gases, argon and neon, the X-ray measurements used have not been on free atomic systems. The emission lines used to calculate IP's for the removal of inner-shell electrons were obtained from the emission spectra of atoms in crystals. The wavelength and shape of these lines will, of course, be affected by the chemical structure of the solids. The lines involving the outermost shells of the atom will be most affected. This chemical effect, for the systems considered here, appears to be small and about the same order of magnitude as the accuracy of the experimental measurements. For example, the full width at half-maximum of the $K\beta_{1,3}$ line of $Cl^-$ in KCl, with no correction made for the unresolved doublet $KM_{II}$ and $KM_{III}$, has been experimentally determined by Deslattes(50) to be 1.00 ± 0.05 eV. Deslattes estimates that 0.4 eV = 0.015 Hartree of this width is attributable to solid-state effects (i.e., the band structure of the 3p band of $Cl^-$). This is to be compared with the wavelength of the line, as measured by Valasek,(51) which is 4394.91 ± 0.14 XU = 103.464 ± 0.003 Hartrees. [The conversion from XU's to A's, as given in Sections 13 and 68 of Sandström's review article,(52) is 1000 XU = (1.00202 ± 0.00002) A.] The wavelength shift of the $K\beta_1$ (or $K\beta_{1,3}$) line of $Cl^-$ as measured in various substances is also small. Valasek(51,53) gives 4394.90 ± 0.07 XU for $Cl^-$ in NaCl, 4394.91 ± 0.14 XU for $Cl^-$ in KCl, and 4394.61 XU for $Cl^-$ in $CaCl_2$. The results of an earlier measurement of the $K\beta_1$ line of $Cl^-$ in the same substances, given by Lindh and Lundquist,(54) are 4394.2 XU, 4394.1 XU, and 4394.2 XU, respectively.

In several cases, the results of more than one measurement of the same line were available. Our choice of which result to use was generally guided by the choices made by Sandström* and Landolt-Börnstein(48) for their compilations of X-ray emission lines. When measurements were made for an atom in several compounds, the values for the atom in an alkali halide compound were usually used. The sources of the experimental data for the X-ray emission lines used are the following: $F^-$, $K\alpha_{1,2}$ Tyrén;(55) Ne, $K\alpha_{1,2}$ Moore and Chalklin;(56) $Na^+$, $K\alpha_{1,2}$ Johnson;(57) $Cl^-$, $K\alpha_1$ and $K\alpha_2$ Shearer;(58) $K\beta_1$ Valasek;(51) $L\eta$ and $L\ell$ Siegbahn and Magnusson;(59) Ar, $K\alpha_1$, $K\alpha_2$, and $K\beta_1$ Lindh and Nilsson;(60) $L\eta$ and $L\ell$ Bačkovský and Dolejšek;(61) $K^+$, $K\alpha_1$ Siegbahn and Dolejšek;(62) $K\alpha_2$ Sandström;* $K\beta_1$ Parrat and Jossem;(63) and $L\eta$ and $L\ell$ Tyrén.(64)

Unfortunately, the method described above cannot be used to determine the IP for removal of a 2s electron from the argon-like ions. According to Sandström* and Landolt-Bornstein,(48) no X-ray emission lines are observed that involve transitions from the 2s-hole state for atoms between chromium and sulfur.

Landolt-Bornstein(48) give a table of the normal energy levels of atoms in which they include values for the 2s-hole ($L_I$) levels of chlorine and potassium. The levels in this table were determined using a combination of X-ray emission lines and absorption limits. The procedure for determining the levels is much like that discussed above, except that X-ray absorption limits of atoms in crystals, rather than optical series limits of free atoms, are used. The values given for the 2s-hole states of chlorine and potassium were not obtained directly from experimental data; they are interpolations made by Tomboulian and Cady.(65) The interpolation was based on rules for the $L_I$-$L_{II}$ (2s-hole, $^2S_{1/2}$ - 2p-hole, $^2P_{1/2}$) screening-doublet splitting.

The levels in the Landolt-Bornstein table may not be used directly as IP's of free atoms because the zero of energy chosen for the atom in the crystal is not the same as the zero of energy of the free atom.(66)

The correction for the 2s-hole IP that must be made to account for the different zeros of energy was determined by comparing the normal energy level given by Landolt-Bornstein for the 2p-hole, $^2P_{1/2}(L_{II})$ state with the IP obtained as described above. The 2s-hole experimental IP's, IP(exp), of $Cl^-$ and $K^+$ given in Table XVIII are the Landolt-Bornstein values, with the corrections -0.17 and +0.56 Hartree, espectively. These values are included only to give a rough indication of the experimental values.

When the experimental IP's are compared with the IP's obtained from the SCF wave functions, the experimental values should be corrected for relativistic effects. The SCF functions were calculated using a

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*See Ref. 52, Section 53. See also the discussion of the accuracy of measurements of X-ray emission spectra in Sections 50-52 in Ref. 52.

nonrelativistic, electrostatic Hamiltonian. The total experimental energy of a system $E_{exp}$ may be written as

$$E_{exp} = E_{nr} + E_{rel}, \tag{23}$$

where $E_{nr}$ is the exact energy eigenvalue of the Hamiltonian of Eq. (10), and $E_{rel}$ is the relativistic correction to the total energy. (To be precise, the reduced mass of the electron should be used in the nonrelativistic Hamiltonian, and mass-polarization corrections should be included in $E_{rel}$.) Then the nonrelativistic IP, IP(nr), is

$$\mathrm{IP(nr)} = E_{nr}(\mathrm{ion}) - E_{nr}(\mathrm{parent}) = \mathrm{IP(exp)} - \Delta\mathrm{IP(rel)}, \tag{24}$$

and

$$\Delta\mathrm{IP(rel)} = E_{rel}(\mathrm{ion}) - E_{rel}(\mathrm{parent}), \tag{25}$$

where ΔIP(rel) is the relativistic correction to IP(exp). The term ion is used here to refer to the system after an electron has been removed from the parent.

For the 1s-hole IP of an atom, ΔIP(rel) is assumed to be equal to the relativistic correction to the IP of the two-electron ion of that atom (IP for $1s^2$ to $1s^1$). Pekeris,(46) using his extremely accurate nonrelativistic wave functions, has calculated the relativistic corrections to the IP's of the two-electron ions of hydrogen through neon. His calculations include the mass polarization correction, relativistic corrections to order $\alpha^2$, and the Lamb shift corrections to order $\alpha^3$. Scherr and Silverman,(67) using an expansion in powers of $Z^{-1}$, have extrapolated Pekeris's calculations to calcium (Z = 20). The results of Pekeris and Scherr and Silverman have been used for ΔIP(rel) for the 1s-hole IP's.

For the 2p-hole IP of an argon-like ion, ΔIP(rel) is assumed to be equal to the relativistic correction to the IP of the ten-electron ion (IP for $1s^22s^22p^6$ to $1s^22s^22p^5$). Scherr, Silverman, and Matsen(47) have calculated these corrections using screened nuclear charges to evaluate the Dirac one-electron energy and the one-electron Lamb shift to order $\alpha^3$.

For the 2p-hole IP's of the neon-like ions and the 3p-hole IP's of the argon-like ions, the only relativistic correction made is that IP(exp) in Table XVIII is given for the center of gravity of the $^2P$ term of the ion. No relativistic corrections are given for the 2s-hole IP's of the neon-like ions and the 2s- and 3s-hole IP's of the argon-like ions.

In several cases, IP(exp), given in Table XVIII, is determined in more than one way; this is done to indicate roughly the reliability of the experimental data. When the different ways give different values of

IP(nr), the method used to obtain IP(nr) is indicated. A correction for the finite mass of the nucleus is included in IP(nr), but not in IP(exp). This correction affects the values of IP(exp) and IP(nr) by no more than two units in the last place given.

The IP of a system can be calculated in two ways from SCF wave functions. One way is to use the frozen-orbital approximation. In the frozen-orbital approximation, an SCF calculation is performed for the parent system, and the SCF orbitals of the parent are also used as the orbitals of the ion. In this approximation, the IP for the removal of an electron from the $n\ell$-shell of a closed-shell system$^2$ is $-\epsilon_{n\ell}$; this result is known as Koopmans's theorem. The second way is to perform separate SCF calculations for the parent and the ion. In this case, the IP is the difference of the SCF energies $\Delta E_{SCF}$ of the two systems. The accurate-set SCF functions of Tables I-IV have been used to calculate the IP in these two ways. The results, IP($-\epsilon_{n\ell}$) and IP($\Delta E_{SCF}$), are given in Table XVIII together with their differences with IP(exp), or with IP(nr) when IP(nr) is given.

The true value of a quantity, in the sense that it is used in the following discussion, is the exact nonrelativistic value obtained from solutions of the Hamiltonian of Eq. (10). The error of an approximate value of a quantity is the error with respect to this true value. The values of IP(exp) or IP(nr) given in Table XVIII 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 in Table XVIII show that when an electron is removed from the outermost shell (2p shell of the neon-like ions, and 3p shell of the argon-like ions), IP($-\epsilon_{n\ell}$) is a better approximation than IP($\Delta E_{SCF}$) to the true IP. The frozen-orbital wave function for the ion is always a poorer approximation than the SCF wave function to the true wave function of the ion. For the lowest state of a symmetry species, the error in the energy of the ion in the frozen-orbital approximation must be larger than the correlation energy of the ion (the error of the SCF energy of the ion). However, in the cases mentioned above, the correlation energy of the parent is more nearly equal to the error in the energy of the ion in the frozen-orbital approximation than to the correlation energy of the ion. The errors in the energies of the parent and ion more nearly cancel, and IP($-\epsilon_{n\ell}$) is a better approximation than IP($\Delta E_{SCF}$) to IP(nr).

The error in the energy of the ion in the frozen-orbital approximation is usually larger than the correlation energy of the parent. Because of this, IP($-\epsilon_{n\ell}$) is usually larger than the true IP. This is not always the case; for $K^+$, IP($-\epsilon_{3p}$) is 0.06 eV smaller than IP(exp) for the removal of a 3p electron.

Note that IP($-\epsilon_{n\ell}$) is larger than the true IP when an inner-shell electron has been removed. If the ion is not in the lowest state of a symmetry species, it is not necessary that the expectation value of the energy for an approximate wave function be an upper bound to the true energy. If the expectation value of the energy in the frozen-orbital approximation for ions in these states was not larger than the true energy, then IP($-\epsilon_{n\ell}$) would be considerably smaller than the true IP.

When an electron is removed from any but the outermost shell, IP($\Delta E_{SCF}$) is a better approximation than IP($-\epsilon_{n\ell}$) to the true IP. When an electron is removed from an inner shell (1s shell of the neon-like ions, and 1s, 2s, or 2p shell of the argon-like ions), the SCF orbitals of the ion are considerably different from the SCF orbitals of the parent (cf., $\langle r \rangle$ and $\langle r^2 \rangle$ in Tables XIII and XIV). Consequently, the error in using the orbitals of the closed-shell parent for these ions is quite large.

The SCF orbitals of the states that 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. The IP($-\epsilon_{n\ell}$) was a good approximation to the IP for the removal of an outermost p electron, but not for an outermost s electron. For these s-hole states, there is another reason why IP($-\epsilon_{n\ell}$) is a poorer approximation than IP($\Delta E_{SCF}$). As discussed in Section IV-A, these s-hole states are likely to be the lowest $^2S$ states of even parity of their ionic systems. The only states for which this is at all in doubt are F(2s-hole) and Cl(3s-hole). When the ion is the lowest state of a symmetry species, IP($-\epsilon_{n\ell}$) must be greater than IP($\Delta E_{SCF}$). Now, IP($\Delta E_{SCF}$) for the removal of an outermost s electron is already larger than the true IP. Since IP($\epsilon_{n\ell}$) must be still larger, it is a poorer approximation to the true IP. The surprising fact that IP($\Delta E_{SCF}$) is larger than the true IP is discussed in Section G below.

The agreement of IP($\Delta E_{SCF}$) with IP(nr) for the removal of an inner-shell electron is remarkably good. [Comparisons of IP($\Delta E_{SCF}$) with IP(nr) for the removal of a 2s electron from an argon-like ion cannot be made since there is no accurate experimental data available.] The error of IP($\Delta E_{SCF}$), for these cases, is always less than 0.2% and often no more than 0.1%. Thus, IP($\Delta E_{SCF}$) 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. Since the error of the HF treatment of the outer-shell orbitals can be expected to be roughly the same whether the inner-shell electron is present or not, $IP(\Delta E_{SCF})$ for the removal of an inner-shell electron should give reasonably good agreement with the true IP.

Thus, $IP(\Delta E_{SCF})$ for the removal of a 2s electron from an argon-like ion should be in good agreement with the true nonrelativistic IP. The relativistic correction to these IP's, estimated from the data of Scherr, Silverman, and Matsen,(47) is probably no more than 0.1 Hartree. Even without relativistic corrections, the values of $IP(\Delta E_{SCF})$, given in Table XVIII, should agree with the correct experimental values to within 1%; because of the relativistic corrections, they should be smaller than the correct experimental values. No direct experimental data are available for these 2s-hole IP's; the values of IP(exp), given in Table XVIII, were obtained through interpolation.(65)

## G. Anomalous Behavior of the Correlation Energy

The correlation energies of some of the hole-state systems have anomalous values. The correlation energy $E_{corr}$ is the error of the total SCF energy $E_{SCF}$ and is defined by the relation

$$E_{nr} = E_{SCF} + E_{corr}, \tag{26}$$

where $E_{nr}$ is the exact nonrelativistic solution of the Hamiltonian of Eq. (10). The sign has been chosen so that $E_{corr}$ is negative for all the systems considered here and is always negative for the lowest state of a symmetry species. It follows immediately from Eq. (26) that

$$IP(nr) - IP(\Delta E_{SCF}) = E_{corr}(ion) - E_{corr}(parent). \tag{27}$$

The error of $IP(\Delta E_{SCF})$, given in the last column of Table XVIII, is the difference of $E_{corr}$ between the parent and the ion.

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

When an electron is removed from the outermost s shell, $IP(\Delta E_{SCF})$ is larger than the true IP. The magnitude of $E_{corr}$ of $Ne^{+}$(2s-hole) is 0.84 eV larger than the magnitude of $E_{corr}$ of neon; $|E_{corr}|$ of $Ar^{+}$(3s-hole) is 3.95 eV larger than $|E_{corr}|$ of argon.

When an electron is removed from the 2p or the 1s shell of one of the argon-like ions, $|E_{corr}|$ of the resulting ion is also larger than $|E_{corr}|$ 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 $|E_{corr}|$ is larger than these uncertainties.

This anomalous behavior of the correlation energy is extremely important in light of the recent work of Clementi(41,68) and in particular of Allen, Clementi, and Gladney(69) to obtain semiempirical rules for the calculation of $E_{corr}$. 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. The analysis of Allen, Clementi, and Gladney is based on a decomposition of $E_{corr}$ into pair-correlation energies. For atoms, the pair-correlation energy is denoted by $E_{corr}(n, \ell, m_\ell, m_s;\ n', \ell', m_\ell', m_s')$, where $n, \ell, m_\ell, m_s$ are the usual one-electron quantum numbers. Allen et al.(69) explicitly make the following three assumptions about this decomposition: (1) The total correlation energy is, to a very good approximation, the sum of the pair-correlation energies,

$$E_{corr} = \Sigma\, E_{corr}(n, \ell, m_\ell, m_s;\ n', \ell', m_\ell', m_s'). \tag{28}$$

(2) The most important pair-correlation energies are for electrons which differ only in their spin quantum numbers, and these correlation energies are independent of $m_\ell$; i.e., $E_{corr}(n, \ell, m_\ell, \alpha;\ n, \ell, m_\ell, \beta) = E_{corr}(n, \ell, \alpha;\ n, \ell, \beta)$. (3) The pair-correlation energy, with only minor qualifications, is a function only of the 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, discussed above, shows that the third assumption is not correct.

From the assumptions and Eq. (27), it follows that when an electron is removed from a closed shell with quantum numbers $n\ell$,

$$-E_{corr}(n, \ell, \alpha;\ n, \ell, \beta) \cong E_{corr}(\text{ion}) - E_{corr}(\text{parent}) = IP(nr) - IP(\Delta E_{SCF}). \tag{29}$$

For neon, Allen, Clementi, and Gladney find that $-E_{corr}(2p\alpha, 2p\beta) \cong +1.7$ eV, $-E_{corr}(2s\alpha, 2s\beta) \cong +3.2$ eV, and $-E_{corr}(1s\alpha, 1s\beta) \cong +1.2$ eV. The results given in Table XVIII show that $E_{corr}(Ne^+; 2p\text{-hole}) - E_{corr}(Ne) = +1.75$ eV, $E_{corr}(Ne^+; 2s\text{-hole}) - E_{corr}(Ne) = -0.84$ eV, and $E_{corr}(Ne^+; 1s\text{-hole}) - E_{corr}(Ne) = +0.65$ 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 $|E_{corr}|$ of ~3.2 eV; but, in fact, $|E_{corr}|$ increases by 0.84 eV. When a 1s electron is removed, they predict a decrease of ~1.2 eV, but there is a decrease of only half that. Allen, Clementi, and Gladney also give pair correlations for fluorine and sodium. Their predictions for the correlation energies of the $n\ell$-hole states of $F^-$ and $Na^+$ are very similar to their predictions for neon.

Clearly the values that the Allen, Clementi, and Gladney analysis gives for $E_{corr}(2s\alpha,2s\beta)$ and $E_{corr}(1s\alpha,1s\beta)$ are not correct. Kestner(70) has considered the anomalous correlation energy of $Ne^+$(2s-hole) using the formalism of Sinanoğlu. He claims that he has accounted for the increase of $|E_{corr}|$ to the accuracy of his calculation.

Kestner explains that the anomalous correlation energy of the 2s-hole state of neon is due to the increased importance of configuration interaction for the SCF function of this state. The $1s^2 2s 2p^6$ configuration of the 2s-hole state of $Ne^+$ can interact with the configurations $1s^2 2s^2 ep^4 ns$, $1s^2 2s 2p^5 np$, and $1s^2 2s^2 2p^4 nd$. The configurations $1s^2 2s^2 2p^6$ and $1s^2 2s^2 2p^5$ of neutral neon and the 2p-hole state of neon can interact only with configurations formed by exciting two electrons into orbitals with principal quantum numbers $n > 2$. The energies of some of the excited configurations that mix with the SCF configuration of the 2s-hole state of neon are closer to the energy of that state, than the energies of the exicted configurations for neon and $Ne^+$(2p-hole) are to the energies of these states. Thus, the mixing of configurations will be larger for the 2s-hole state than for the neutral atom or the 2p-hole state. When 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 argon-like ions. It will be interesting to see if Kestner's treatment can account for the increase of $|E_{corr}|$ for these states. The increase of $|E_{corr}|$ for these states is more than four times as large as the increase of $|E_{corr}|$ for the 2s-hole states of the neon-like ions.

# V. TRANSITION PROBABILITIES BETWEEN THE SCF WAVE FUNCTIONS

## A. Theory

To calculate electric-dipole transition probabilities, it is necessary to evaluate matrix elements I of the form

$$I = \langle \Psi_I | \Sigma \underset{\sim}{r}(i) | \Psi_F \rangle, \tag{30}$$

where $\Psi_I$ and $\Psi_F$ are the normalized many-electron wave functions of the initial and final states, $\underset{\sim}{r}(i)$ is the position vector of the $i^{th}$ electron, and the sum is over all the electrons in the atom. In this calculation, $\Psi_I$ and $\Psi_F$ are approximated by SCF wave functions. For the states considered here, the SCF function is given by a single Slater determinant and is an eigenfunction of $L^2$ and $S^2$, but not $J^2$. Since $\Psi_I$ and $\Psi_F$ were obtained as separate SCF solutions of the variational equations, the SCF one-electron orbitals for the two states have no special relation to each other. In particular, the overlap integrals of the orbitals $\phi^{(I)}_{n\ell m}$ of $\Psi_I$ with the orbitals $\phi^{(F)}_{n'\ell m}$ of $\Psi_F$ are not zero or one; that is, $\langle \phi^{(I)}_{n\ell m} | \phi^{(F)}_{n'\ell m} \rangle \neq \delta_{n,n'}$.

It is common practice(45,71,72) to approximate the dipole transition matrix element I of Eq. (30) by

$$I = \langle \Psi_I | \Sigma \underset{\sim}{r}(i) | \Psi_F \rangle \cong \underset{\sim}{W} \int_0^\infty P^{(I)}_{n\ell}(r) \, r \, P^{(F)}_{n'\ell'}(r) \, dr. \tag{31}$$

Here $P^{(I)}_{n\ell}$ and $P^{(F)}_{n'\ell'}$ are the radial wave functions of the active electron (the electron making the transition) for the initial and final states. The radial functions $P^{(I)}_{n\ell}$ and $P^{(F)}_{n'\ell'}$ need not be SCF functions.(45,71) The vector $\underset{\sim}{W}$ includes the angular integrations and also depends on the symmetry species and subspecies of the initial and final states. The approximation of Eq. (31) is equivalent to assuming that the orthonormality relations

$$\langle \phi^{(I)}_{n\ell m} | \phi^{(F)}_{n'\ell m} \rangle = \int_0^\infty P^{(I)}_{n\ell}(r) \, P^{(F)}_{n'\ell}(r) \, dr = \delta_{n,n'} \tag{32}$$

hold. We shall refer to this approximation as the active electron approximation.

With SCF functions, or with any total wave functions which are expressed as combination of Slater determinants, it is not necessary to use the active electron approximation. Löwdin(73) has given an expression for the matrix element of a one-electron operator $\Sigma O(i)$ between two arbitrary Slater determinants, $\Psi_U$ and $\Psi_V$. Löwdin showed that

$$<\Psi_U|\Sigma O(i)|\Psi_V> = \Sigma_{k,\ell}<\psi_k^{(U)}(1)|O(1)|\psi_\ell^{(V)}(1)>D_{UV}(k|\ell), \tag{33}$$

where $\psi_k^{(U)}$ and $\psi_\ell^{(V)}$ are spin-orbitals of the determinants $\Psi_U$ and $\Psi_V$ respectively, the double sum $\overline{k, \ell}$ is over all the occupied spin-orbitals, and $D_{UV}(k|\ell)$ is the signed minor, formed by removing the kth row and $\ell$th column, of the matrix $D_{UV}$. The elements of $D_{UV}$ are the overlap integrals between the spin-orbitals of the two determinants; the $k\ell$ element of $D_{UV}$ is

$$(D_{UV})_{k\ell} = <\psi_k^{(U)}|\psi_\ell^{(V)}>. \tag{34}$$

The SCF spin-orbitals were defined in Eq. (2).

The evaluation of the sum in Eq. (33) is simple because the SCF spin-orbitals are symmetry-adapted and because there is only radial function for each shell [cf., Eqs. (2) and (5)]. In fact, for the transitions considered, it was never necessary to evaluate a determinant larger than 3 x 3. The dipole transition matrix elements required for this calculation were, therefore, evaluated by means of Eq. (33).

The results of the dipole transition calculations will be given as total absolute multiplet strengths $S(M)_{IF}$. In the electric dipole approximation, $S(M)_{IF}$ is defined, in atomic units, by

$$S(M)_{IF} = \sum_{M_S,M_S'} \sum_{M_L,M_L'} |<\Psi_I(L,S,M_L,M_S)|\Sigma\underset{\sim}{r}(i)|\Psi_F(L',S,M_L',M_S')>|^2, \tag{35}$$

where L, S, $M_L$, and $M_S$ are the usual orbital and spin angular momentum quantum numbers for the many-electron system. The sum is over all the states of the initial and final terms. This sum need not be evaluated explicitly; sum rules* for the sum over $M_L$ and $M_L'$, and the fact that the operator $\Sigma\underset{\sim}{r}(i)$ does not involve the spin, may be used to reduce the sum. For the case of interest here (transitions between $^2S$ and $^2P$ states with $\Delta L = 1$), $S(M)_{IF}$ becomes

$$S(M)_{IF} = (2S+1)(L+1)(2L+3)|<\Psi_I(L+1,S,M_L=L,M_S=S)|\Sigma z(i)|\Psi_F(L,S,M_L=L,M_S=S)>|^2, \tag{36}$$

where z(i) is the z coordinate of the ith electron.

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*Feenberg and Pake(74) present a complete statement and derivation of the sum rules.

Absolute line strengths may be obtained from $S(M)_{IF}$ by using the relative strengths of lines in multiplets. Oscillator strengths and spontaneous transition probabilities may also be obtained from $S(M)_{IF}$ by using either experimental or SCF transition energies. Summaries of current notation and definitions of terms may be found elsewhere.(75) The general problem of emission and absorption of radiation is treated in detail elsewhere; see, for example, Bethe and Salpeter.(20)

For the sake of convenience, we give here the relations that will be required later for the discussion of the width of the 1s-hole state; this width is referred to as the K-state width, or simply the K width.

The absolute line strength $S(L)_{IF}$ is defined, in atomic units, by

$$S(L)_{IF} = \sum_{M_J, M_J'} |\langle \Psi_I(J, L, S, M_J) | \Sigma \underset{\sim}{r}(i) | \Psi_F(J', L', S, M_J') \rangle|^2. \tag{37}$$

The subscripts I and F for $S(L)_{IF}$ refer to levels (i.e., ${}^{2S+1}L_J$), while the subscripts for $S(M)_{IF}$ refer to terms (i.e., ${}^{2S+1}L$). For the transitions of interest here, $S(L)_{IF}$ is given in terms of $S(M)_{IF}$ by

$$\left.\begin{array}{ll} {}^2S_{1/2} \longleftrightarrow {}^2P_{1/2}; & S(L)_{IF} = (1/3)S(M)_{IF} \\ {}^2S_{1/2} \longleftrightarrow {}^2P_{3/2}; & S(L)_{IF} = (2/3)S(M)_{IF}. \end{array}\right\} \tag{38}$$

The transition probability for spontaneous emission of a photon $A_{IF}$ is given, in $\sec^{-1}$, by

$$A_{IF} = 2.1419 \times 10^{10} \, [(\Delta E_{IF})^3/g_I] \, S_{IF}(L), \tag{39}$$

where $\Delta E_{IF} = E_I - E_F$ is the energy of the line in atomic units, $S_{IF}(L)$ is in atomic units, and $g_I$ is the degeneracy of the initial level.

The total width of a level I, $\Gamma_I$, may be written as $\Gamma_I = \hbar P_I$, where $P_I$ is the total probability of transitions from the level I to all lower-lying levels. The partial width due to radiative transitions $\Gamma^{(R)}$, called the radiative width, is

$$\Gamma_I^{(R)} = \hbar \sum_F A_{IF}, \tag{40}$$

where the sum is over all levels with lower energy, $E_F < E_I$. For inner-shell hole states, where radiationless transitions are important, the total width is given by

$$\Gamma_I = \Gamma_I^{(R)} + \Gamma_I^{(A)}, \tag{41}$$

where $\Gamma_I^{(A)}$ is called the Auger width. The fluorescence yield $\varpi_I$, the fraction of the total transition rate due to radiative transitions, may be written as

$$\varpi_I = \Gamma_I^{(R)} \Big/ \left[\Gamma_I^{(R)} + \Gamma_I^{(A)}\right] = \Gamma_I^{(R)}/\Gamma_I. \tag{42}$$

These matters are discussed in detail elsewhere.(76)

The operator $\Sigma\underset{\sim}{r}(i)$ is called the dipole length operator. It is possible, through the use of commutation relations, to find alternate expressions for the dipole transition matrix element of Eq. (30). For the many-electron Hamiltonian of Eq. (10), we have the relations

$$[\Sigma\underset{\sim}{r}(k),\mathscr{H}] = i\Sigma\underset{\sim}{p}(k) = \Sigma\underset{\sim}{\nabla}(k), \tag{43a}$$

and

$$[\Sigma\underset{\sim}{p}(k),\mathscr{H}] = -i[\Sigma\underset{\sim}{\nabla}(k)]\mathscr{V} = -iZ\Sigma\underset{\sim}{r}(k)/r(k)^3, \tag{43b}$$

where $Z$ is the nuclear charge and the commutation relations are expressed in atomic units. If $\Psi_I$ and $\Psi_F$ are exact eigenfunctions of $\mathscr{H}$, the dipole transition matrix element I, in atomic units, may be evaluated, using Eq. (30) or equivalently, as either

$$I = \langle\Psi_I|[-1/\Delta E_{IF}]\Sigma\underset{\sim}{\nabla}(k)|\Psi_F\rangle, \tag{44a}$$

or

$$I = \langle\Psi_I|[Z/(\Delta E_{IF})^2]\Sigma\underset{\sim}{r}(k)/r(k)^3|\Psi_F\rangle, \tag{44b}$$

where $\Delta E_{IF} = E_I - E_F$ is the difference between the <u>exact</u> nonrelativistic total energies of the initial and final states. The operators in Eqs. (44a) and (44b) are called the dipole-velocity and dipole-acceleration operators, respectively. Note that the dipole-acceleration operator was obtained from the exact many-electron potential energy and not from some average one-electron potential.

When a dipole transition matrix element is evaluated using approximate wave functions (e.g., SCF functions), the length, velocity, and acceleration forms of the matrix element will not have the same value. The values obtained using the three operators do not necessarily bound the correct value of the matrix element. Even if the three values are in close agreement, they are not necessarily correct. However, the main contributions to the matrix element come from different regions of r for the three operators. The contributions to the value of the matrix element from comparatively large r are most important for the dipole length operator, from intermediate values of r for the velocity operator, and from small values of r for the acceleration operator. Thus, if the three operators give approximately equal values for a transition matrix element, it is not unreasonable to infer that these values are close to the true value. In any event, it is interesting to see how the results obtained using the length, velocity, and acceleration operators compare. Such a comparison will be made in Section B below.

## B. Results of the Dipole Transition Probability Calculations

A computer program was written for the IBM 704 to calculate all the one-electron overlap and electric-dipole transition integrals, between the expansion SCF orbitals of two states, needed for the evaluation of $S(M)_{IF}$. The one-electron overlap and transition integrals are defined in Eqs. (33) and (34). Transition integrals may be computed for the dipole-length, -velocity, and -acceleration operators. Since the angular integration follows immediately from the properties of the spherical harmonics, only the radial portions of the transition integrals are calculated by the program. For the transitions reported here, the program was modified to calculate $S(M)_{IF}$ directly, with the electric dipole transition matrix element evaluated exactly, as a matrix element between the many-electron SCF wave functions. Actually, $S(M)_{IF}$ is calculated when the length operator is used; but $(\Delta E_{IF})^2 S(M)_{IF}$ and $(\Delta E_{IF})^4 Z^{-2} S(M)_{IF}$ are calculated when the velocity and acceleration operators are used. In this way, experimental, rather than SCF, energy differences may be used when the velocity and acceleration forms of $S(M)_{IF}$ are evaluated.

For a given transition, the input to the transition moment program consists of two sets of punched cards. One of these sets contains the information necessary to describe the SCF function of the initial state; the other, the information necessary to describe the final state. While a set of cards may be prepared manually, it is available, optionally, as part of the output of an SCF calculation performed with the 7094 SCF program.

The values of $S(M)_{IF}$, in the electric dipole approximation, for all possible electric dipole transitions between the $n\ell$-hole states computed, are presented in Table XIX. The matrix elements were computed exactly, between many-electron SCF wave functions, using the expression of

Eq. (33). The matrix elements were evaluated using the dipole-length operator. The SCF functions used are the accurate-set functions reported in Tables I-IV. The values of $S(M)_{IF}$ are given in atomic units.

TABLE XIX. Total Absolute Multiplet Strengths $S(M)_{IF}$ for Transitions between the $n\ell$-hole States of $F^-$, Ne, $Na^+$, $Cl^-$, Ar, and $K^+$. (Values of $S(M)_{IF}$ are in a.u.)

| | F | $Ne^+$ | $Na^{++}$ |
|---|---|---|---|
| 2s-hole → 2p-hole<br>ultraviolet emission line | 2.0652 | 1.4632 | 1.0855 |
| 1s-hole → 2p-hole<br>Kα emission line | 0.02466 | 0.02193 | 0.01937 |
| | Cl | $Ar^+$ | $K^{++}$ |
| 3s-hole → 3p-hole<br>ultraviolet emission line | 5.3584 | 4.1392 | 3.2995 |
| 2p-hole → 3s-hole<br>$L\ell, \eta$ emission lines | 0.03430 | 0.02808 | 0.02324 |
| 2s-hole → 3p-hole<br>not observed | 0.02932 | 0.02991 | 0.02965 |
| 2s-hole → 2p-hole<br>not observed | 0.3382 | 0.2923 | 0.2549 |
| 1s-hole → 3p-hole<br>Kβ emission line | 0.0006722 | 0.0007010 | 0.0007078 |
| 1s-hole → 2p-hole<br>Kα emission line | 0.009245 | 0.008354 | 0.007588 |

For most of the transitions given in Table XIX, $S(M)_{IF}$, for a given transition, decreases with increasing Z. Along an isoelectronic sequence, the wave functions for a given state become more contracted as the nuclear charge increases (cf., $\langle r \rangle$ and $\langle r^2 \rangle$ given in Tables XIII and XIV). Thus, the main contributions to the dipole transition matrix element $\langle \Psi_I \| \Sigma_i \underset{\sim}{r}(i) \| \Psi_F \rangle$ come from smaller values of r for larger values of Z, and $S(M)_{IF}$ becomes smaller with increasing Z. In fact, for the hydrogenic one-electron ions, $S(M)_{IF}$ goes as $1/Z^2$.

For the 1s-hole → 3p-hole and the 2s-hole → 3p-hole transitions of Cl, $Ar^+$, and $K^{++}$, however, $S(M)_{IF}$ does not have this behavior; for the 1s-hole → 3p-hole transition, $S(M)_{IF}$ increases with increasing Z. Although all the SCF orbitals of a given state contract with increasing Z, the 3p orbitals contract more than the 1s or 2s orbitals. The region of important "overlap," the region where $\Psi_I^* \Psi_F$ is large, will increase, and, in some cases, this increase will be more important than the fact that the "overlap" occurs in a region of smaller r. As Z becomes larger, the contraction with increasing Z, of all the orbitals of a given state, becomes more nearly the same. For large enough Z, $S(M)_{IF}$ for any transition should decrease with increasing Z along an isoelectronic sequence; $S(M)_{2s\text{-hole},3p\text{-hole}}$ is smaller for $K^{++}$ than for $Ar^+$, and it is likely that $S(M)_{1s\text{-hole},3p\text{-hole}}$ will be smaller for $Ca^{+3}$ than for $K^{++}$.

For transitions between the $n\ell$-hole states of neon and argon, Table XX compares the effects, on $S(M)_{IF}$, of the use of several different approximations for the evaluation of the dipole transition matrix element. The results for these transitions are very similar to the results for the transitions of the other atoms. The values of $S(M)_{IF}$ are given for the dipole length, velocity, and acceleration operators defined by Eqs. (30) and (44). For each operator, the transition matrix element was evaluated using the many-electron expression of Eq. (33), and also using the active-electron approximation of Eq. (31).

The notation $\langle \Psi(ns\text{-hole}) | \underset{\sim}{Q} | \Psi(n'p\text{-hole}) \rangle$ is used in Table XX to indicate that the matrix element for $S(M)_{ns\text{-hole},n'p\text{-hole}}$ was evaluated between many-electron SCF wave functions. In the active-electron approximation,

$$S(M)_{ns\text{-hole},n'p\text{-hole}} = 6 \left| \langle \phi^{(ns\text{-hole})}_{n'p,m=0} | O_z | \phi^{(n'p\text{-hole})}_{ns,m=0} \rangle \right|^2; \qquad (45)$$

where

$$O_z^{(\ell)} = z,$$

$$O_z^{(v)} = -(1/\Delta E_{IF}) \frac{\partial}{\partial z},$$

and

$$O_z^{(a)} = [Z/(\Delta E_{IF})^2][z/r^3]. \qquad (46)$$

The notation $\langle \phi^{(I)}_{n\ell} | \underset{\sim}{Q} | \phi^{(F)}_{n'\ell'} \rangle$ is used in Table XX to indicate that the matrix element for $S(M)_{IF}$ was evaluated using the active-electron approximation; for simplicity, the subscript m for the symmetry subspecies is not used. Matrix elements were evaluated in the active-electron approximation in two ways: first, using the appropriate orbitals from the SCF wave functions for the initial and final states of the transition, as indicated in Eq. (45); and second, using the orbitals from the SCF wave function for the closed-shell system, either neutral neon or argon.

TABLE XX. Total Absolute Multiplet Strengths $S(M)_{IF}$ Using Several Approximations for the Dipole Transition Matrix Element [$S(M)_{IF}$ and $\Delta E_{IF}$ are in a.u.]

| Transition | Approximation for Matrix Element | Operator | | | | |
|---|---|---|---|---|---|---|
| | | Length | Velocity | Diff.* | Acceleration | Diff.* |
| Ne$^+$; 2s-hole → 2p-hole<br>$\Delta E_{IF}$ = 0.9877 | $\langle\Psi(\text{2s-hole})\|\underset{\sim}{Q}\|\Psi(\text{2p-hole})\rangle$ | 1.463 | 1.166 | 20.3% | ~150. | . . . |
| | $\langle\varphi_{2p}^{(\text{2s-hole})}\|\underset{\sim}{Q}\|\varphi_{2s}^{(\text{2p-hole})}\rangle$ | 1.465 | 1.181 | . . . | | |
| | $\langle\varphi_{2p}^{(\text{Ne})}\|\underset{\sim}{Q}\|\varphi_{2s}^{(\text{Ne})}\rangle$ | 1.630 | 1.282 | . . . | | |
| Ne$^+$; 1s-hole → 2p-hole<br>$\Delta E_{IF}$ = 39.151 | $\langle\Psi(\text{1s-hole})\|\underset{\sim}{Q}\|\Psi(\text{2p-hole})\rangle$ | 0.02193 | 0.01979 | 9.8% | 0.02252 | 2.7% |
| | $\langle\varphi_{2p}^{(\text{1s-hole})}\|\underset{\sim}{Q}\|\varphi_{1s}^{(\text{2p-hole})}\rangle$ | 0.02119 | 0.02066 | . . . | 0.02355 | . . . |
| | $\langle\varphi_{2p}^{(\text{Ne})}\|\underset{\sim}{Q}\|\varphi_{1s}^{(\text{Ne})}\rangle$ | 0.01549 | 0.01415 | . . . | 0.01484 | . . . |
| Ar$^+$; 3s-hole → 3p-hole<br>$\Delta E_{IF}$ = 0.4932 | $\langle\Psi(\text{3s-hole})\|\underset{\sim}{Q}\|\Psi(\text{3p-hole})\rangle$ | 4.139 | 4.791 | 15.8% | ~3000. | . . . |
| | $\langle\varphi_{3p}^{(\text{3s-hole})}\|\underset{\sim}{Q}\|\varphi_{3s}^{(\text{3p-hole})}\rangle$ | 4.143 | 4.798 | . . . | | |
| | $\langle\varphi_{3p}^{(\text{Ar})}\|\underset{\sim}{Q}\|\varphi_{3s}^{(\text{Ar})}\rangle$ | 4.460 | 4.777 | . . . | | |
| Ar$^+$; 2p-hole → 3s-hole<br>$\Delta E_{IF}$ = 8.067 | $\langle\Psi(\text{2p-hole})\|\underset{\sim}{Q}\|\Psi(\text{3s-hole})\rangle$ | 0.02808 | 0.02150 | 23.4% | wrong sign** | . . . |
| | $\langle\varphi_{3s}^{(\text{2p-hole})}\|\underset{\sim}{Q}\|\varphi_{2p}^{(\text{3s-hole})}\rangle$ | 0.02492 | 0.02222 | . . . | 0.000003 | . . . |
| | $\langle\varphi_{3s}^{(\text{Ar})}\|\underset{\sim}{Q}\|\varphi_{2p}^{(\text{Ar})}\rangle$ | 0.01981 | 0.01835 | . . . | wrong sign** | . . . |
| Ar; 2s-hole → 3p-hole<br>$\Delta E_{IF}$ = 11.357 | $\langle\Psi(\text{2s-hole})\|\underset{\sim}{Q}\|\Psi(\text{3p-hole})\rangle$ | 0.02991 | 0.02413 | 19.3% | 0.01056 | 64.7% |
| | $\langle\varphi_{3p}^{(\text{2s-hole})}\|\underset{\sim}{Q}\|\varphi_{2s}^{(\text{3p-hole})}\rangle$ | 0.02893 | 0.02547 | . . . | 0.01213 | . . . |
| | $\langle\varphi_{3p}^{(\text{Ar})}\|\underset{\sim}{Q}\|\varphi_{2s}^{(\text{Ar})}\rangle$ | 0.01954 | 0.01701 | . . . | 0.00562 | . . . |
| Ar$^+$; 2s-hole → 2p-hole<br>$\Delta E_{IF}$ = 2.796 | $\langle\Psi(\text{2s-hole})\|\underset{\sim}{Q}\|\Psi(\text{2p-hole})\rangle$ | 0.2923 | 0.2079 | 28.9% | ~ 50. | . . . |
| | $\langle\varphi_{2p}^{(\text{2s-hole})}\|\underset{\sim}{Q}\|\varphi_{2s}^{(\text{2p-hole})}\rangle$ | 0.2842 | 0.2054 | . . . | | |
| | $\langle\varphi_{2p}^{(\text{Ar})}\|\underset{\sim}{Q}\|\varphi_{2s}^{(\text{Ar})}\rangle$ | 0.2967 | 0.2262 | . . . | | |
| Ar$^+$; 1s-hole → 3p-hole<br>$\Delta E_{IF}$ = 116.72 | $\langle\Psi(\text{1s-hole})\|\underset{\sim}{Q}\|\Psi(\text{3p-hole})\rangle$ | 0.0007010 | 0.0006519 | 7.0% | 0.0007061 | 0.7% |
| | $\langle\varphi_{3p}^{(\text{1s-hole})}\|\underset{\sim}{Q}\|\varphi_{1s}^{(\text{3p-hole})}\rangle$ | 0.0005358 | 0.0005433 | . . . | 0.0006001 | . . . |
| | $\langle\varphi_{3p}^{(\text{Ar})}\|\underset{\sim}{Q}\|\varphi_{1s}^{(\text{Ar})}\rangle$ | 0.0004223 | 0.0004011 | . . . | 0.0004118 | . . . |
| Ar$^+$; 1s-hole → 2p-hole<br>$\Delta E_{IF}$ = 108.16 | $\langle\Psi(\text{1s-hole})\|\underset{\sim}{Q}\|\Psi(\text{2p-hole})\rangle$ | 0.008354 | 0.008003 | 4.2% | 0.008683 | 3.9% |
| | $\langle\varphi_{2p}^{(\text{1s-hole})}\|\underset{\sim}{Q}\|\Psi_{1s}^{(\text{2p-hole})}\rangle$ | 0.008470 | 0.008347 | . . . | 0.009082 | . . . |
| | $\langle\varphi_{2p}^{(\text{Ar})}\|\underset{\sim}{Q}\|\varphi_{1s}^{(\text{Ar})}\rangle$ | 0.007607 | 0.007208 | . . . | 0.007482 | . . . |

*This is the percent difference between $S(M)_{IF}$ evaluated using the length operator, and $S(M)_{IF}$ evaluated using the velocity or acceleration operator.

**The sign of the transition matrix element for the acceleration operator is not the same as the sign of the matrix element for the length operator.

The second case (the use of the SCF orbitals of a single state for the wave functions of both the initial and final states of a transition) may be regarded as a frozen-orbital approximation for $S(M)_{IF}$. It is, in a sense, similar to the use of Koopmans's Theorem for the IP of a system. In this case, the active-electron approximation gives the correct value for the transition matrix element since the orthonormality conditions $<\phi^{(I)}_{n\ell m}|\phi^{(F)}_{n'\ell m}> = \delta_{n,n'}$ are satisfied.

In Table XX, the superscript on the $\phi$ indicates the state for which the orbital was computed. The entry "wrong sign" in the table means that the sign of the transition matrix element for the acceleration operator was not the same as the sign for the length operator; for exact eigenfunctions, the signs must be the same.

The nonrelativistic energy differences $\Delta E_{IF}$ were obtained by taking differences of the IP's given in Table XVIII; IP(exp) was used for the 3p- and 3s-hole states of the argon-like ions, and the 2p- and 2s-hole states of the neon-like ions; IP(nr) was used for the 2p-hole states of the argon-like ions, and for all the 1s-hole states; and IP($\Delta E_{SCF}$) was used for the 2s-hole states of the argon-like ions.

The calculations were performed using the accurate-set SCF functions given in Tables I-IV. The values of $S(M)_{IF}$ and $\Delta E_{IF}$ are given in atomic units. The column labeled "Diff." is the difference between $S(M)_{IF}$ evaluated using the dipole-length operator, and $S(M)_{IF}$ evaluated using the dipole-velocity or -acceleration operator. This difference is only given when the dipole matrix elements for $S(M)_{IF}$ have been computed between the many-electron SCF wave functions.

For all but one of the transitions given in Table XX, the dipole-length form of $S(M)_{IF}$ obtained using the orbitals of the closed-shell system (third line and first column for each transition) gives a significantly poorer result than that obtained using the orbitals for the initial and final states of the transition (first and second lines and first column for each transition). For the 3s-hole → 3p-hole transition of $Ar^+$, the improvement is 8%; for the 1s-hole → 3p-hole transition of $Ar^+$, the improvement is 40%. Only for the 2s-hole → 2p-hole transition of $Ar^+$ is the improvement as small as 1.5%.

For the dipole-velocity form of $S(M)_{IF}$, the frozen-orbital approximation sometimes gives a better result than the use of the SCF functions of the initial and final states of the transition. Here, we mean better in the sense of being more nearly equal to the dipole-length value of $S(M)_{IF}$ with the many-electron matrix element correctly evaluated. However, the agreement in these cases between the length and velocity forms of $S(M)_{IF}$ is not very good, and the better result of the frozen-orbital approximation does not have much meaning.

It seems, from the results given in Table XX, that the use of the SCF functions of the initial and final states of a transition gives a significantly better value for $S(M)_{IF}$ than the use of the frozen-orbital approximation.

In several cases, the value of $S(M)_{IF}$ obtained when the dipole transition matrix element is evaluated between total many-electron wave functions is quite different from the value obtained when the active-electron approximation is used. The difference is largest for transitions between the 1s-hole and the outermost p-hole states; it is smallest, and quite negligible, for transitions between the outermost s-hole and outermost p-hole states. The value of the many-electron matrix element cannot be much different from the active-electron approximation value unless the minors $D_{IF}(k\|\ell)$, defined in Eqs. (33) and (34), are considerably different from one or zero. This condition is met for the former transitions, but not for the latter, where the orbitals of the initial and final states are too similar.

Note that the value of $S(M)_{IF}$ obtained using the many-electron expression for the matrix element is often larger than that obtained using the active-electron approximation. It has been suggested(77,78) that the correct evaluation of the matrix element simply corrects the active-electron approximation for overlap effects. If this were true, then the many-electron expression for the matrix element would always give a smaller result than the active-electron approximation since overlap effects always introduce a factor less than one. In several cases, transition integrals between orbitals other than the transition integral of the active-electron approximation must make significant contributions to the value of the matrix element. The best example of this is the 1s-hole → 3p-hole transition of $Ar^+$, where the value of dipole length form of $S(M)_{IF}$ using the many-electron matrix element is 30% larger than value in the active electron approximation.

In discussing the use of the length, velocity, and acceleration forms of the dipole matrix element, we will consider only the cases where the matrix element is evaluated between the many-electron SCF functions of the initial and final states. That is, of the values of $S(M)_{IF}$ in Table XX, only the values in the first row of each transition will be compared.

The values of the length and velocity forms of $S(M)_{IF}$ are always at least in reasonable, if not necessarily good, agreement. In the worst case, the 2s-hole → 2p-hole transition of $Ar^+$, the velocity form of $S(M)_{IF}$ is 30% smaller than the length form.

The acceleration form of $S(M)_{IF}$ often has absurd values. For several transitions, the acceleration form of $S(M)_{IF}$ is larger than the length and velocity forms by a factor of between 100 and 1000; and for one transition, the sign of the acceleration form of the matrix element, Eq. (44b), is different from the signs of the length and velocity forms of the matrix element, Eqs. (30) and (44a). However, for transitions from 1s-hole states, the acceleration form of $S(M)_{IF}$ is in good agreement with the length and velocity forms. For the 1s-hole → 2p-hole transition of $Ne^+$ and the 1s-hole → 3p-hole transition of $Ar^+$, the difference between the length and acceleration forms of $S(M)_{IF}$ is, in fact, less than the difference between the length and velocity forms.

When the agreement between the length and acceleration forms of $S(M)_{IF}$ is good, the important one-electron transition integrals are between orbitals with simple structure. The orbitals involved either have no radial nodes (i.e., 1s and 2p), or the contribution to the value of the integral from the region around and past the radial node is small (i.e., 1s and 3p). When the important, one-electron transition integrals are between orbitals whose nodal structure is important in determining the value of the integral, the acceleration form of $S(M)_{IF}$ has poor values.

For transitions between outer-shell hole states, one might consider using some screened, effective, nuclear charge, $Z_{eff}$, for the acceleration form of the dipole transition matrix element. In place of Eq. (44b), the expression

$$I \cong \langle \Psi_I \| [Z_{eff}/(\Delta E_{IF})^2] \Sigma \underset{\sim}{r}(k)/r(k)^3 \| \Psi_F \rangle \tag{47}$$

would be used. For the 3s-hole → 3p-hole transition of $Ar^+$, $Z_{eff} = 0.7$ would be required to bring the length and acceleration forms of $S(M)_{IF}$ into agreement; for the 2s-hole → 2p-hole transition of $Ne^+$, $Z_{eff} = 1$ would be required. However, a reasonable value of $Z_{eff}$ for these cases, based on arguments about the screening of the nuclear charge by the electron charge distribution (e.g., Slater's rules), must be $Z_{eff} \gtrsim 2$. Thus, even the use of a $Z_{eff}$ will not give good values for the acceleration form of $S(M)_{IF}$.

The length form of the dipole transition matrix element has the advantage of being less sensitive than the velocity or acceleration forms to the precise shape of the approximate wave functions. The velocity operator involves derivatives of the orbitals, and the acceleration operator varies strongly and weighs different regions of r very differently. From these considerations, it would seem best to use the length form of the matrix element to evaluate $S(M)_{IF}$.

Chandrasekhar(79) has pointed out that larger values of r are more important for the evaluation of the length form of the dipole matrix element than for the evaluation of the total energy; conversely, smaller values of r are more important for the evaluation of the acceleration form of the matrix element than for the evaluation of the energy. Thus, Chandrasekhar suggests that the velocity form of the matrix element is the most suitable form when the wave functions used have been obtained from an application of the variational principle.

He used the three forms of the matrix element for the calculation of transitions from the ground state to continuum states of the $H^-$ ion. The use of the velocity form of the matrix element did, indeed, give better results. But, 6- and 12-term Hylleraas-type functions were used for the ground-state wave function of $H^-$. These functions are considerably more accurate than HF functions, and the conclusion above may not apply when HF wave functions are used to evaluate the transition matrix elements.

Weiss(80) has calculated oscillator strengths for several transitions of helium. He compared the results, for both the length and velocity forms of the matrix element, obtained by using HF functions and by using the more accurate Hylleraas-type functions. For all but three of these transitions, when HF wave functions were used, the value obtained with the length form of the matrix element was more accurate than that obtained with the velocity form. For two transitions, the use of the velocity form of the matrix element gave very poor results, while the results obtained with the length form were quite accurate. In the three cases in which the use of the velocity form of the matrix element gave better results, both the length and velocity forms gave good results; in these cases, the largest difference between the results obtained using the length and velocity forms with the HF wave functions was less than 5%. Bates and Damgaard(71) have compared the length and velocity forms of the multiplet strength, calculated using HF functions, with experimental values for several transitions of lithium and sodium. In all the cases they considered, the length form of the multiplet strength, although it sometimes gave poor values, was in better agreement with experiment than the velocity form. These calculations would seem to bear out the expectation that the use of the length form of the matrix element, when HF wave functions are used, will give more reliable results than the use of the velocity form.

The simple basis set SCF functions, given in Tables V-VIII, have also been used to calculate $S(M)_{IF}$. The agreement between the values obtained using the accurate-set SCF functions and the simple set SCF functions is quite good. For the length form of $S(M)_{IF}$, the differences between the values obtained using the simple and accurate set functions are never larger than 0.35%; for the velocity form of $S(M)_{IF}$, the differences are never larger than 0.10%. The greatest differences between the simple set and accurate set SCF orbitals are at the tails of the orbitals (c.f., Tables IX-XII). It is not surprising, then, that the differences for the velocity form of $S(M)_{IF}$ are sometimes less than those for the length form. For the acceleration form of $S(M)_{IF}$, the differences are somewhat larger than for the length and velocity forms, but only for the 2p-hole → 3s-hole transitions of Cl, $Ar^+$, and $K^{++}$ is the agreement rather poor.

Varsavsky,(47) using a method based on screened nuclear charges, gives values of $S(M)_{IF}$ for a large number of ultraviolet transitions. Varsavsky's values and the values obtained from this calculation are compared in Table XXI. The values of $S(M)_{IF}$ given for this calculation are taken from Table XIX. Varsavsky's values are all approximately twice as large as the values of this calculation. It seems likely that he made an error of a factor of 2 in calculating $S(M)_{IF}$ from the value of the radial integral $\int_0^\infty P_{np}^{(I)} r\, P_{ns}^{(F)}\, dr$. The values of $S(M)_{IF}$ are, as usual, in atomic units.

TABLE XXI. Comparison of $S(M)_{IF}$ with Calculations by Varsavsky (Values of $S(M)_{IF}$ are in a.u.)

| 2s-hole → 2p-hole | | | |
|---|---|---|---|
| | F | $Ne^+$ | $Na^{++}$ |
| This calculation | 2.065 | 1.463 | 1.086 |
| Varsavsky* | 5.011 | 2.991 | 1.977 |
| **3s-hole → 3p-hole** | | | |
| | Cl | $Ar^+$ | $K^{++}$ |
| This calculation | 5.36 | 4.14 | 3.30 |
| Varsavsky* | 11.53 | 8.30 | 6.23 |

*See Ref. 45.

Experimental data for the absolute or relative intensities of the X-ray lines computed here have not been found. However, a calculation of $\Gamma_K^{(R)}$, the radiative width of the 1s-hole state (or K state), can provide a comparison with experiment.

For the argon-like ions, 1s-hole → 2p-hole (Kα) and the 1s-hole → 3p-hole (Kβ) transitions make the most important contributions to $\Gamma_K^{(R)}$. All other transitions from the 1s-hole state involve at least double excitations (e.g., $1s2s^22p^63s^23p^6 \rightarrow 1s^22s^22p^63s3p^5ns$, $n \geq 4$) and are much less probable.

The value of $\Gamma_K^{(R)}$ for argon has been calculated using the values of $S(M)_{IF}$ given in Table XIX, the experimental values for the energies of the Kα and Kβ emission lines(62) [$\Delta E(K\alpha_1) = 108.70$ Hartrees, $\Delta E(K\alpha_2) = 108.62$ Hartrees, and $\Delta E(K\beta_1) = 117.26$ Hartrees], and the relations of Eqs. (38-40). The value is found to be $\Gamma_K^{(R)} = 0.0835$ eV. The K-shell fluorescence yield for argon, as determined by Watanabe, Schnopper, and Cirillo,(81) is $\bar{\omega}_K$ = 0.140 ± 0.014. From Eq. (42), a value of the total width of the K-state $\Gamma_K$ = 0.60 ± 0.06 eV is obtained. The uncertainty in $\Gamma_K$ is taken entirely from the uncertainty in the value of $\bar{\omega}_K$. Table XXII compares this value of $\Gamma_K$ and values obtained directly from experimental data on X-ray emission and absorption by Watanabe(80) and by Deslattes.(52) The value which we have obtained is, within experimental uncertainties, in agreement with the experimental values.

TABLE XXII. A Comparison of Several Values of $\Gamma_K$ for Argon

| Author | $\Gamma_K$ (eV) |
|---|---|
| Present Work | 0.60 ± 0.06 |
| Watanabe* | 0.68 ± 0.03 |
| Deslattes** | 0.70 ± 0.05 |

*See Ref. 78.

**See Ref. 50.

## ACKNOWLEDGMENTS

The author gratefully acknowledges many helpful discussions with, and encouragement from, Professor C. C. J. Roothaan and Dr. T. L. Gilbert, who jointly sponsored this research. He is indebted to Dr. Gilbert for pointing out the anomalous behavior of the correlation energy of the 2s-hole state of neon, and to Dr. A. J. Freeman for having suggested these calculations.

The author wishes to thank Dr. O. C. Simpson and the Solid State Science Division for their hospitality during his stay at Argonne National Laboratory. The author wishes to acknowledge that preliminary work, at The University of Chicago, on this publication was supported by the Advanced Research Projects Agency through the U. S. Army Research Office (Durham), under Contract No. DA-11-ORD-022-3119, and by a grant from the National Science Foundation.

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*Some care should be taken in using those IP's, given in this paper, that have been obtained from X-ray data. The conversion factor for wavelength from k XU's to A's, 1 k XU = 1.00202 A, has been neglected; and most of the X-ray term levels given in Table II are too large by this factor.

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