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# Analytic Hartree-Fock Wave Functions for the 3$p$-Shell Atoms

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Hartree-Fock wave functions have been obtained for the 3$p$-row atoms, i.e., for neutral Al, Si, P, S, Cl, and Ar, and for $Cl^-$. Solutions were determined in analytic form using a version of Nesbet's symmetry and equivalence restrictions to simplify the calculations for atoms with both closed and unclosed shells of the same $l$ value. These restrictions, the reason for their use, and their relation to other open-shell methods are discussed and the calculated one-electron wave functions and their eigenvalues are presented.

## I. INTRODUCTION

ONE of the most successful schemes for approximating solutions of the many-electron Schrödinger equation is the one-electron approximation. Its applications have been many and varied and have included properties of atoms, molecules, and solids. But basic to the scheme is the assumption that one has available one-electron wave functions, called orbitals, whose description depends only on the coordinates of a single particle. Well-defined and useful orbitals (and in many ways the most accurate) are those determined by a self-consistent field solution of the Hartree-Fock (H-F) equations for free atoms. In our own investigations we have found these functions to be conspicuously absent for the unfilled 3$p$-shell atoms[1] and this has led us to determine Hartree-Fock solutions for $Cl^-$ and the neutral atoms Al, Si, P, S, Cl, and Ar. These are conventional or restricted Hartree-Fock solutions in that one-electron functions of the same shell are constrained to have the same radial dependence.[2] Analytic methods were used utilizing a version of Nesbet's symmetry and equivalence restrictions[3]; details of the method are discussed in the sections that follow.

Aside from their own inherent interest as a description of the electronic structure of free atoms, a major purpose of such calculations is to supply a starting point for further investigations. The results to be reported here have already been utilized in a number of investigations: Atomic scattering factors have been obtained[4] for these atoms and particularly for Al in an attempt to account for the discrepancy between the theoretical and the experimental x-ray form factor recently obtained[5] for the metal; an investigation[6,7] of the effect of self-consistent solutions for the Sternheimer quadrupole polarizabilities[8] of ions has utilized the $Cl^-$ results; the Si results and basis set have been used in an effort to improve on the core and valence electron self-consistency in orthogonalized plane wave calculations[9] for silicon; Al wave functions were needed and employed in a theoretical study[10] of the observed negative Knight shifts in rare-earth aluminum intermetallic compounds[11]; and finally, the P and Cl results have furnished a starting point for an investigation[12] into the effects associated with the unrestricted Hartree-Fock formalism (i.e., no requirement on common radial behavior of orbitals).

In what follows, we will first concentrate on the symmetry and equivalence restrictions,[8] why we use them, and their effect. Secondly, we will report the results, but will keep the discussion of these to a minimum. Their relation to experiment is similar to that already seen[13] for the unfilled 3$d$-shell iron-series ions and we will not repeat the observations here. We have supplied enough results so that the interested reader can make similar comparisons if he so wishes.

## II. SYMMETRY AND EQUIVALENCE RESTRICTIONS IN THE ANALYTIC HARTREE-FOCK METHOD

There are certain difficulties associated with obtaining Hartree-Fock solutions for an atom with both closed and unclosed shells of the same $l$ value. This can

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1 Boys and Price [S. F. Boys and V. E. Price, Phil. Trans. Roy. Soc. A246, 451 (1954)] have obtained analytic functions with exchange for S, $S^-$, and Cl utilizing configuration interaction and simple atomic orbitals.

2 See R. E. Watson and A. J. Freeman, Phys. Rev. **120**, 1125 (1960), for a recent review discussion of the Hartree-Fock method and the restrictions usually associated with its application to many-electron systems.

3 R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955).

4 A. J. Freeman and R. E. Watson, Acta Cryst. (to be published).

5 B. W. Batterman, D. R. Chipman, and J. J. DeMarco, Phys. Rev. **122**, 68 (1961).

6 A. J. Freeman and R. E. Watson, Bull. Am. Phys. Soc. **6**, 166 (1961).

7 R. E. Watson and A. J. Freeman (to be published).

8 R. M. Sternheimer, Phys. Rev. **84**, 244 (1951).

9 F. Quelle (to be published).

10 R. E. Watson and A. J. Freeman, Phys. Rev. Letters **6**, 277, 388(E) (1961).

11 V. Jaccarino, B. J. Mathias, M. Peter, H. Suhl, and J. H. Wernick, Phys. Rev. Letters **5**, 251 (1960).

12 R. E. Watson and A. J. Freeman (to be published).

13 R. E. Watson, Phys. Rev. **118**, 1036 (1960), and *ibid.* **119**, 1934 (1960).

best be illustrated by a specific example. Consider the $1s^22s^22p^63s^2\ 3p^2,{}^3P$ state of neutral Si where $L=M_L=1$ and $S=M_S=1$. The Hartree-Fock many-electron wave function can be written as a single Slater determinant[14] (with the two $3p$ orbitals having $\alpha$ spin and $m_l$ values of $+1$ and 0) provided that the various one-electron functions are orthonormal *and* that there is a single radial wave function per shell. This gives us the conventional or "restricted" Hartree-Fock wave function. The second requirement is, in fact, a restriction on the wave function[15] and on the Hartree-Fock formalism. The Hartree-Fock equations are obtained by applying the variation principle to the total energy of the system. We will consider the case of an energy computed for a many-electron Hamiltonian consisting of kinetic energy, nuclear potential energy, and inter-electronic electrostatic energy. Applying the variational principle in conjunction with the requirement of a single radial function per shell yields a single ("restricted") Hartree-Fock equation per shell which is the *average* of those which could be derived for the different *occupied* orbitals of that shell. For Si, the restricted Hartree-Fock equation (in its integrated form) for the $2p$ shell is

$$\begin{aligned}\epsilon_{2p}=K_{2p}&+2F^0(2p,1s)+2F^0(2p,2s)+2F^0(2p,3s)\\&+6F^0(2p,2p)+2F^0(2p,3p)\\&-G^0(2p,1s)-G^0(2p,2s)-G^0(2p,3s)\\&-G^0(2p,2p)-(2/5)G^2(2p,2p)\\&-(1/3)G^0(2p,3p)-(2/15)G^2(2p,3p).\end{aligned}\tag{1}$$

The $3p$ equation can be written

$$\begin{aligned}\epsilon_{3p}=K_{3p}&+2F^0(3p,1s)+2F^0(3p,2s)+2F^0(3p,3s)\\&+6F^0(3p,2p)+2F^0(3p,3p)\\&-G^0(3p,1s)-G^0(3p,2s)-G^0(3p,3s)\\&-G^0(3p,2p)-(2/5)G^2(3p,2p)\\&-G^0(3p,3p)-(1/5)G^2(3p,3p).\end{aligned}\tag{2}$$

The $\epsilon_i$'s are the one-electron energies, the $K_i$'s are one-electron kinetic+nuclear potential energy integrals and the $F^k$'s and $G^k$'s are the Slater Coulomb and exchange integrals.[16] The two equations are identical [i.e., Eq. (1) can be obtained by inserting $2p$ for $3p$ as the first parameter in each term in Eq. (2)] *except* for the coefficients multiplying the $G^k(i,3p)$ terms of the last lines. If these coefficients were the same, the $2p$ and $3p$ would be different eigenfunctions of the same equation and thus automatically orthogonal, but since these coefficients are different, a self-consistent solution of Eqs. (1) and (2) will yield *nonorthogonal* $p$-wave functions. Different coefficients exist because of our requirement of a single radial function per shell; $p$ orbitals differing in $m_l$ and/or $m_s$ interact differently with the unfilled shell (note that orbitals of the same $l$, $m_l$, and $m_s$ but different $n$ have identical *individual* H-F equations). The average for the full shell is different than that for two orbitals in the $3p$ shell and thus the differing coefficients occur. The counterparts to Eqs. (1) and (2) for all the atoms of the $3p$ series are given in the Appendix.

There are three ways one can obtain orthogonal analytic Hartree-Fock orbitals for cases like neutral Si:

(i) One can add a Lagrange multiplier to ensure $2p$-$3p$ orthogonality.[14] Roothaan[17] and Huzinaga[18] have shown how such Lagrange multipliers can be incorporated into the analytic H-F method. The strength of this approach is that it straightforwardly applies the conventional method of adding restrictions to a set of equations while maintaining a single radial orbital per shell. This scheme utilizes a three-electron supermatrix as compared with the two-electron supermatrix of earlier[19] analytic methods and makes applications much more cumbersome.

(ii) The most obvious method of obtaining orthogonality is to relax the restriction which led to nonorthogonality. If we had gotten separate (averaged) Hartree-Fock solutions for (1) those $2p$ orbitals with $m_l$ and $m_s$ in common with the occupied $3p$ orbitals and (2) those not in common, we would have a set of orthonormal Hartree-Fock orbitals for Si. We would, of course, then have two distinct $2p$ radial functions. One could solve even less restricted "unrestricted" Hartree-Fock equations, retaining orthonormality and obtaining larger numbers of differing radial orbitals. Since this is the least restricted of the three approaches, it yields the wave function of lowest total energy and thus *in principle* is the best many-electron wave function. The method involves the simultaneous solution of more Hartree-Fock equations than (i) [or (iii) below] but avoids the three-electron supermatrix of (i). One disadvantage of this scheme is that the resulting many-electron function is not an exact eigenfunction of $L$ and/or $S$. While this may not be serious for some uses,[20] such a function can be a treacherous starting point for certain computations (e.g., configuration interaction or the use of perturbation theory). Properly symmetrized (thus many-determinantal) "unrestricted" Hartree-Fock many-electron functions are difficult to solve for variationally. None, in fact, have been obtained to date. This matter is discussed elsewhere.[2,21]

(iii) A third approach is to use a version of Nesbet's[8]

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

[15] An atomic system with a net spin and/or angular momentum will provide an environment with which electrons of the same shell but differing $m_s$ and/or $m_l$ will interact differently. In other words, separate Hartree-Fock solutions for them would yield different radial orbitals.

[16] For definitions see E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1953), p. 177.

[17] C. C. J. Roothaan, Revs. Modern Phys. **32**, 179 (1960).

[18] S. Huzinaga, Phys. Rev. **120**, 866 (1960).

[19] C. C. J. Roothaan, Revs. Modern Phys. **23**, 69 (1951).

[20] W. Marshall (to be published) has given such an argument; see also N. Bessis, H. Lefebvre-Brion, and C M. Moser (to be published).

[21] R. K. Nesbet and R. E. Watson, Ann. Phys. **9**, 260 (1960).

TABLE I. Parameters ($A_j$ and $Z_j$) which define the basis functions ($R_j$).

| $R_j$'s used for the construction of | $j$ | $A_j$ | $Z_j$ for Al | Si | P | S | Cl | Ar | $Cl^-$ |
|---|---|---|---|---|---|---|---|---|---|
| $s$ orbitals ($l=0$) | 1 | 0 | 14.5168 | 15.6334 | 16.7500 | 17.8666 | 18.9832 | 20.0999 | 18.9832 |
| | 2 | 0 | 11.3133 | 12.1835 | 13.0537 | 13.9239 | 14.7941 | 15.6644 | 14.7941 |
| | 3 | 1 | 10.8561 | 11.8216 | 12.7871 | 13.7526 | 14.7181 | 15.6838 | 14.7181 |
| | 4 | 1 | 6.8933 | 7.5755 | 8.2577 | 8.9398 | 9.6220 | 10.3041 | 9.6220 |
| | 5 | 1 | 4.6860 | 5.2061 | 5.7262 | 6.2464 | 6.7665 | 7.2867 | 6.7665 |
| | 6 | 2 | 4.1147 | 4.6712 | 5.2277 | 5.7842 | 6.3407 | 6.8971 | 6.2190 |
| | 7 | 2 | 2.0500 | 2.3810 | 2.7121 | 3.0431 | 3.3742 | 3.7052 | 3.2450 |
| | 8 | 2 | 1.3196 | 1.5647 | 1.8098 | 2.0549 | 2.2999 | 2.5450 | 2.1679 |
| | 9 | 2 | 0.8363 | 0.9866 | 1.1369 | 1.2872 | 1.4375 | 1.5878 | 1.3550 |
| $p$ orbitals ($l=1$) | 10 | 0 | 9.8219 | 10.8139 | 11.8059 | 12.7980 | 13.7900 | 14.7820 | 13.7900 |
| | 11 | 0 | 6.1873 | 6.8493 | 7.5114 | 8.1734 | 8.8355 | 9.4975 | 8.8355 |
| | 12 | 0 | 3.8452 | 4.2336 | 4.6220 | 5.0103 | 5.3987 | 5.7870 | 5.3987 |
| | 13 | 1 | 3.1870 | 3.3949 | 3.6028 | 3.8107 | 4.0186 | 4.2264 | 4.0186 |
| | 14 | 1 | 1.4804 | 1.7195 | 1.9586 | 2.1976 | 2.4367 | 2.6757 | 2.4367 |
| | 15 | 1 | 0.9972 | 1.1824 | 1.3676 | 1.5528 | 1.7380 | 1.9232 | 1.6382 |
| | 16 | 1 | 0.5003 | 0.5932 | 0.6861 | 0.7790 | 0.8720 | 0.9649 | 0.8219 |

symmetry and equivalence restrictions. For Si this would consist of solving Eq. (2) (or its counterpart for other ions) for *both* the $2p$ and $3p$ shells.[22] The resulting computations represent a considerable economy in computer time over (i) and (ii). A small error, associated with outer electron ($3p$) exchange, is introduced into an inner electron ($2p$) equation. This approximation is reasonable because inner electrons are insensitive to both the exchange and the more important Coulomb effects of outer electrons. There are many situations[23] where this insensitivity has been utilized. The best test of (iii) is to compare the energy of the resulting total wave function with those of (i) and (ii). Unrestricted Hartree-Fock calculations[11] for neutral P and Cl indicate that an improvement of about 0.0015 ry out of total energies of $-700$ to $-900$ ry is associated with going from (iii) to (ii).[21,24] Calculations for[21] Li suggest that roughly half of this energy improvement is obtained on going from (iii) to (i). This energy difference, of about 0.0007 ry, is roughly one-tenth of one percent of the difference (often called the "correlation energy"[25]) between the Hartree-Fock total energy and the exact eigenvalue of our many-electron Hamiltonian.

In what follows, we are reporting calculations using method (iii). We believe that these are of sufficient accuracy for the restricted Hartree-Fock method and that if one requires better many-electron eigenvalues or eigenfunctions he should consider the "unrestricted" Hartree-Fock formalism, or better yet some description which goes beyond the "simple" one-electron approach.

[22] No advantage (in total energy) was obtained by using a compromise between the $G^k(i,3p)$ coefficients of Eqs. (1) and (2). This contrasts with the Li case of reference 21.

[23] Three such are: (1) The frequent use of core functions, obtained for one atomic state, in calculations for other atomic states, (differing in configuration and/or state of ionization), (2) the success of the Slater rules [J. C. Slater, Phys. Rev. **36**, 57 (1930)] for providing simple atomic orbitals (these presume no outer orbital effect on inner orbitals) and (3) the use of free atom functions as core functions in energy band calculations.

[24] A. J. Freeman, Revs. Modern Phys. **32**, 273 (1960) has made similar observations in a molecular problem.

[25] P. O. Löwdin, *Advances in Chemical Physics*, edited by I. Prigogine (Interscience Publishers, Inc., New York), Vol. 2, p. 207 (1959).

## III. ANALYTIC HARTREE-FOCK METHOD

The analytic H-F method uses matrix techniques to obtain orthonormal analytic Hartree-Fock radial orbitals, $U_i(r)$, of the form:

$$U_i(r)=\sum_j C_{ij}R_j(r). \tag{3}$$

Their normalization condition is

$$\int_0^\infty |U_i(r)|^2dr=1, \tag{4}$$

and the basis functions, $R_j$, are of the form:

$$R_j(r)\equiv N_jr^{(l+A_j+1)}e^{-Z_jr}, \tag{5}$$

where $l$ is the one-electron angular momentum quantum number appropriate for the one-electron orbital of which $U_i(r)$ is the radial part. $N_j$ is a normalization constant and is expressible in terms of the other parameters, i.e.:

$$N_j=[(2Z_j)^{2l+2A_j+3}/(2l+2A_j+2)!]^{\frac{1}{2}}. \tag{6}$$

$U_i(r)$'s of common $l$ value are constructed from a common set of $R_j(r)$'s. Given the basis sets, i.e., the $R_j(r)$'s, the problem is reduced to solving the Hartree-Fock integro-differential equations for the eigenvectors (the $C_{ij}$'s) and their eigenvalues. This is done by straightforward matrix diagonalization and manipulation and avoids the problems of numerical accuracy inherent in the integrations of the numerical Hartree-Fock method.

The problem of basis sets is, however, always associated with the analytic Hartree-Fock method. First there is the question of the size of the set. A small set is desirable because of economy in computer time and

TABLE II. The eigenvectors ($C_{ij}$) defining the Hartree-Fock radial functions ($U_i$) in terms of the basis sets ($R_j$).

| $j$ $i=$ | Al 1s | Si 1s | P 1s | S 1s | Cl 1s | Ar 1s | $Cl^-$ 1s |
|---|---|---|---|---|---|---|---|
| 1 | 0.47820335 | 0.47801597 | 0.47650550 | 0.47433873 | 0.47057770 | 0.46843906 | 0.46853182 |
| 2 | 0.49560163 | 0.49824461 | 0.50252456 | 0.50753060 | 0.51463953 | 0.51923323 | 0.51760183 |
| 3 | 0.05508320 | 0.05194539 | 0.04835136 | 0.04482154 | 0.04037388 | 0.03783273 | 0.03835872 |
| 4 | −0.04176310 | −0.04347004 | −0.04470139 | −0.04625191 | −0.04660228 | −0.04961999 | −0.04255196 |
| 5 | 0.03517378 | 0.03799932 | 0.04028467 | 0.04290337 | 0.04419208 | 0.04835368 | 0.03874278 |
| 6 | −0.01275182 | −0.01408673 | −0.01518227 | −0.01647929 | −0.01712669 | −0.01916713 | −0.01433782 |
| 7 | 0.00328381 | 0.00333849 | 0.00332557 | 0.00343135 | 0.00328116 | 0.00360844 | 0.00293627 |
| 8 | −0.00208467 | −0.00202937 | −0.00196202 | −0.00200526 | −0.00185897 | −0.00205635 | −0.00173223 |
| 9 | 0.00064383 | 0.00057422 | 0.00051826 | 0.00050693 | 0.00043970 | 0.00047650 | 0.00045088 |
| $i=$ | 2s | 2s | 2s | 2s | 2s | 2s | 2s |
| 1 | −0.09989705 | −0.10609487 | −0.11123490 | −0.11613808 | −0.12073746 | −0.12448169 | −0.11231714 |
| 2 | −0.16445991 | −0.16348699 | −0.16299528 | −0.16200474 | −0.16070403 | −0.16002612 | −0.17288020 |
| 3 | −0.13454941 | −0.13861219 | −0.14170556 | −0.14461845 | −0.14728644 | −0.14914618 | −0.13795468 |
| 4 | 0.16844612 | 0.15460438 | 0.14287276 | 0.13339409 | 0.12539405 | 0.11830138 | 0.09623364 |
| 5 | 0.73860189 | 0.73990991 | 0.73992204 | 0.73862683 | 0.73667456 | 0.73399316 | 0.78296249 |
| 6 | 0.25492763 | 0.26642326 | 0.27692571 | 0.28675089 | −0.29569014 | 0.30424846 | 0.27540135 |
| 7 | 0.00818443 | 0.01164115 | 0.01529906 | 0.01867834 | 0.02211865 | 0.02540739 | 0.01661696 |
| 8 | −0.00322537 | −0.00424561 | −0.00522343 | −0.00603379 | −0.00681901 | −0.00751387 | −0.00477546 |
| 9 | 0.00089386 | 0.00114269 | 0.00136969 | 0.00155631 | 0.00173871 | 0.00189119 | 0.00145554 |
| $j$ $i=$ | 3s | 3s | 3s | 3s | 3s | 3s | 3s |
| 1 | 0.03176749 | 0.03558677 | 0.03480513 | 0.03517716 | 0.03226696 | 0.02781904 | 0.04601181 |
| 2 | 0.02535354 | 0.02959468 | 0.03854337 | 0.04486713 | 0.05472073 | 0.06606737 | 0.03205335 |
| 3 | 0.04425760 | 0.04930876 | 0.04799508 | 0.04914036 | 0.04604961 | 0.04216877 | 0.06034449 |
| 4 | −0.06690018 | −0.07277665 | −0.06270257 | −0.06440589 | −0.05545469 | −0.04842645 | −0.07894860 |
| 5 | −0.15116208 | −0.16248240 | −0.18849294 | −0.19367097 | −0.21001735 | −0.22121075 | −0.18009669 |
| 6 | −0.12724852 | −0.15628299 | −0.16772952 | −0.19103485 | −0.20191239 | −0.21396688 | −0.21416129 |
| 7 | 0.28726532 | 0.30330287 | 0.29654439 | 0.30031295 | 0.29052539 | 0.28422188 | 0.40045392 |
| 8 | 0.70009039 | 0.69690759 | 0.70452779 | 0.70460221 | 0.71291582 | 0.71474538 | 0.59959016 |
| 9 | 0.12098648 | 0.12075475 | 0.12683228 | 0.13342544 | 0.14067898 | 0.15173284 | 0.16294774 |
| $i=$ | 2p | 2p | 2p | 2p | 2p | 2p | 2p |
| 10 | 0.04491808 | 0.04082228 | 0.03629017 | 0.03216818 | 0.02815814 | 0.02436348 | 0.02815975 |
| 11 | 0.26567769 | 0.26098350 | 0.26221183 | 0.26455447 | 0.26830322 | 0.27269964 | 0.26812371 |
| 12 | 0.64446107 | 0.68489733 | 0.70895994 | 0.72611248 | 0.73772890 | 0.74583141 | 0.73732558 |
| 13 | 0.11017090 | 0.07026888 | 0.04113520 | 0.01737931 | −0.00340506 | −0.02253016 | −0.00189991 |
| 14 | 0.00536737 | 0.00265586 | 0.00538798 | 0.00985020 | 0.01842689 | 0.02997370 | 0.01551419 |
| 15 | −0.00216351 | −0.00071710 | −0.00236645 | −0.00504626 | −0.00942535 | −0.01484941 | −0.00713564 |
| 16 | 0.00042991 | 0.00014665 | 0.00044655 | 0.00086477 | 0.00147451 | 0.00215452 | 0.00134824 |
| $i=$ | 3p | 3p | 3p | 3p | 3p | 3p | 3p |
| 10 | −0.01080307 | −0.01181046 | −0.01223249 | −0.01305630 | −0.01294533 | −0.01240628 | −0.01158317 |
| 11 | −0.03116521 | −0.03787150 | −0.04151134 | −0.03863229 | −0.03982780 | −0.04249049 | −0.03901622 |
| 12 | −0.14269477 | −0.17923597 | −0.20945233 | −0.24064481 | −0.26254303 | −0.27928565 | −0.23911788 |
| 13 | 0.01360895 | 0.02649990 | 0.04626733 | 0.08715074 | 0.12224880 | 0.15616371 | 0.10276812 |
| 14 | 0.24267490 | 0.34702725 | 0.39674585 | 0.37949215 | 0.35931781 | 0.33196037 | 0.38612138 |
| 15 | 0.69938117 | 0.63306352 | 0.58839757 | 0.57240453 | 0.56879140 | 0.57422563 | 0.49188592 |
| 16 | 0.13470789 | 0.08747425 | 0.07358222 | 0.09455649 | 0.09941246 | 0.09797354 | 0.20319459 |

retains the advantages of wave functions of analytic form. These advantages come from the ease, accuracy, and convenience with which matrix elements can be obtained if the functions are in analytic form. Large basis sets allow greater accuracy of solution (*provided* that we do not have too many basis functions which are too much alike, for then one finds it difficult to obtain accurate matrix diagonalization).[26] The current basis sets represent a compromise between those used in the highly accurate calculations of Roothaan and coworkers[27] for the two-, three-, and four-electron ions and those obtained by one of us[18] for the iron-series ions. The relatively larger basis sets of the current calculations as compared with those for the iron series make them less convenient to utilize in their analytic form (e.g., for multicenter integrals). On the other hand we have greater computational accuracy, accuracy which we believe is slightly superior to the few existing numerical Hartree-Fock calculations for ions of this size. We would like to compare total energies but accurate estimates of these are not available for the other calculations.[28]

[26] P. O. Löwdin, Ann. Rev. Phys. Chem. **11**, 107 (1960).

[27] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Revs. Modern Phys. **32**, 186 (1960).

[28] Another good test is to study $[H_i^{(r)}U_i(r)]/U_i(r)$ as a function of $r$. $H(r)$ is a one-electron Hartree-Fock operator. Unfortunately this test requires virtually the full machinery of the numerical Hartree-Fock method and so is difficult to apply.

TABLE III. Hartree-Fock one-electron energies ($\epsilon_i$), one-electron nuclear potential+kinetic energies ($K_i$), total energies and some Slater two-electron integrals ($G^k$ and $F^k$) for the 3$p$ shell atoms. All energies are in atomic units (1 a.u.=2 ry). Also given are one-electron energies of Ar and $Cl^-$ as obtained by Hartree and Hartree by numerical solution of the Hartree-Fock equations.

| | Al$(3p^1,{}^2P)$ | Si$(3p^2,{}^3P)$ | P$(3p^3,{}^4S)$ | S$(3p^4,{}^3P)$ | Cl$(3p^5,{}^2P)$ | Ar$(3p^6,{}^1S)$ | Ar$(3p^6,{}^1S)$[b] | $Cl^-(3p^6,{}^1S)$ | $Cl^-(3p^6,{}^1S)$[a] |
|---|---|---|---|---|---|---|---|---|---|
| $\epsilon_{1s}$ | −58.4880 | −68.7954 | −79.9553 | −91.9923 | −104.8766 | −118.606 | −118.6 | −104.5092 | $-104.5_5$ |
| $\epsilon_{2s}$ | −4.9069 | −6.1501 | −7.5062 | −8.9996 | −10.6040 | −12.319 | $-12.3_3$ | −10.2329 | $-10.23_5$ |
| $\epsilon_{3s}$ | −0.3940 | −0.5389 | −0.6955 | −0.8785 | −1.0717 | −1.276 | $-1.277_5$ | −0.7356 | −0.727 |
| $\epsilon_{2p}$ | −3.2145 | −4.2500 | −5.3963 | −6.6780 | −8.0688 | −9.568 | $-9.57_5$ | −7.6993 | $-7.69_5$ |
| $\epsilon_{3p}$ | −0.1990 | −0.2965 | −0.3911 | −0.4363 | −0.5051 | −0.589 | $-0.590_5$ | −0.1518 | $-0.1485_5$ |
| $K_{1s}$ | −84.3958 | −97.8912 | −112.3867 | −127.8825 | −144.3785 | −161.875 | | −144.3785 | |
| $K_{2s}$ | −19.6503 | −23.0011 | −26.6005 | −30.4499 | −34.5477 | −38.893 | | −34.5459 | |
| $K_{3s}$ | −5.6520 | −7.0571 | −8.5259 | −10.1057 | −11.7631 | −13.515 | | −11.5565 | |
| $K_{2p}$ | −18.8243 | −22.2069 | −25.8282 | −29.6952 | −33.8057 | −38.162 | | −33.8004 | |
| $K_{3p}$ | −4.3326 | −5.7526 | −7.1916 | −8.6012 | −10.1407 | −11.791 | | −9.5539 | |
| $F^0(3s,3s)$ | 0.34843 | 0.40989 | 0.46764 | 0.52541 | 0.58097 | 0.63541 | | 0.56555 | |
| $F^0(3s,3p)$ | 0.29668 | 0.36369 | 0.42426 | 0.47805 | 0.53242 | 0.58674 | | 0.50075 | |
| $F^0(3p,3p)$ | 0.26286 | 0.33039 | 0.39112 | 0.44114 | 0.49368 | 0.54707 | | 0.45175 | |
| $F^2(3p,3p)$ | 0.13223 | 0.16682 | 0.19754 | 0.22093 | 0.24626 | 0.27234 | | 0.21926 | |
| $G^1(3s,3p)$ | 0.18568 | 0.23502 | 0.27799 | 0.31302 | 0.34935 | 0.38578 | | 0.32094 | |
| Total energy | −241.8692 | −288.8536 | −340.7177 | −397.5031 | −459.4797 | −526.814 | | −459.5750 | |

[a] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A156**, 45 (1936).
[b] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 450 (1938). Note that only the (3$s$), (3$p$) wave functions were obtained by solution of the Hartree-Fock equations; the (1$s$), (2$s$), (2$p$) wave functions were obtained by interpolation between the values for $Ca^{++}$, $K^+$, and $Cl^-$.

Having chosen the size of the basis sets there is the question of choosing the individual $R_j$'s. For a given finite number of such functions there is in principle no unique choice for the basis set. A *series* of Hartree-Fock calculations, in which the $Z_j$ parameters were varied, was used to obtain a "best choice" for the $R_j$'s. The parameters of the resulting basis sets appear in Table I. We have reported (and used) screening constants ($Z_j$'s) with four digits after the decimal point. This does not mean that the $Z_j$'s were uniquely established to this many digits. The investigations of varying $Z_j$'s carried this many digits and since these were kept in the final calculation they are reported in this form. We would estimate that improved, and/or enlarged basis sets would lower the total energies by less than 0.001 ry. Since this is of the order of the change of energy in going from (i) to (iii), it does not seem worthwhile to further improve the energy by improving and/or enlarging the basis set.

Before presenting results, we should reiterate that we are solving the counterpart of Eq. (2) for both the 2$p$ and 3$p$ shells. In the closed shell cases of $Cl^-$ and Ar this makes no difference since the counterparts of Eqs. (1) and (2) are identical in form.

## IV. RESULTS

The eigenvectors ($C_{ij}$) which define the $U_i(R)$'s in terms of the $R_j(r)$'s appear in Table II. Note that the $C_{ij}$'s are given for *normalized* $R_j(r)$'s. The $C_{ij}$'s have not been uniquely established to the number of digits quoted but with these digits they provide well-normalized, well-defined Hartree-Fock orbitals. The total energies, one-electron energies ($\epsilon_i$'s), $K_i$'s, and selected $F^k(i,j)$ and $G^k(i,j)$ integrals appear in Table III. The $\epsilon_{2p}$'s have been evaluated using the counterparts of Eq. (1) and *not* Eq. (2). In order to conserve space the two-electron integrals which are listed were limited to those involving the 3$s$ and/or 3$p$ orbitals. These integrals enter into the Slater-Racah parameterization[29] of the multiplet spectra. If the reader fits the experimental spectra,[30] he will discover systematic discrepancies between computed integrals and the experimental "integrals." Such discrepancies were observed previously for the iron-series ions[12] and arise because correlation effects (i.e., effects beyond the Hartree-Fock formalism) appreciably perturb the multiplet spectra.

Also included in Table III are the $\epsilon_i$'s obtained by the Hartrees in their pioneering numerical calculations for[31] $Cl^-$ and[32] Ar. Except for the $Cl^-$ 3$s$, there is good agreement between the $\epsilon_i$'s for the two sets of calculations. The agreement for Ar is remarkable since in the numerical[32] calculation the inner functions (1$s$, 2$s$, and 2$p$) were obtained by extrapolation and only the outer functions (3$s$, and 3$p$) were solved for by solution of the Hartree-Fock equations.

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[29] See E. U. Condon and G. H. Shortley, reference 16, Chap. VII.
[30] C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards, Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949), Vol. 1.
[31] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A156**, 45 (1936).
[32] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 450 (1938).

the IBM 704 at Avco and we thank the staff at that facility for their cooperation.

## APPENDIX

The counterparts to Eqs. (1) and (2) for the $3p$ series atoms can be written as:

$$\begin{aligned}\epsilon_x = K_x &+ 2F^0(x,1s) + 2F^0(x,2s) + 2F^0(x,3s)\\ &+ 6F^0(x,2p) - G^0(x,1s) - G^0(x,2s) - G^0(x,3s)\\ &- G^0(x,2p) - 2/5G^2(x,2p)\\ &+ qF^0(x,3p) - rG^0(x,3p) - sG^2(x,3p),\end{aligned}$$

where $q$, $r$, and $s$ are coefficients which are different for Eqs. (1) and (2) and are determined by the number, $n$, of electrons in the $3p$ shell. For Eq. (1) they are:

| $n$ | $q$ | $r$ | $s$ |
|---|---|---|---|
| 1 | 1 | −1/6 | −1/15 |
| 2 | 2 | −2/6 | −2/15 |
| 3 | 3 | −3/6 | −3/15 |
| 4 | 4 | −4/6 | −4/15 |
| 5 | 5 | −5/6 | −5/15 |
| 6 | 6 | −1 | −6/15 |

and for Eq. (2) they are:

| $n$ | $q$ | $r$ | $s$ |
|---|---|---|---|
| 1 | 1 | −1 | 0 |
| 2 | 2 | −1 | −0.2 |
| 3 | 3 | −1 | −0.4 |
| 4 | 4 | −1 | −0.3 |
| 5 | 5 | −1 | −0.32 |
| 6 | 6 | −1 | −0.4. |

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# Temperature Variation of Ionic Mobilities in Hydrogen

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Measurements have been made of the temperature variation of the mobilities of positive ions in hydrogen over the range 77°–300°K. The zero-field mobility values are $\mu_0 = 12.3$ cm²/v sec (300°K), 13.3 (195°K), and 13.0 (77°K). The present results at 300°K are in agreement with the data of Lauer, Bradbury, and Mitchell at low $E/p_0$, and at high $E/p_0$ agree with Rose's measurements. Only a single ion species was observed in the present studies. Reasons are given which support the belief that the ion observed in these measurements was $H_3^+$.

## INTRODUCTION

RESULTS of measurements of the mobilities of positive ions in hydrogen reported in the literature date back as early as 1932. Since then, the mobility of positive ions in hydrogen has been the subject of numerous experimental investigations. In spite of this, as a result of discrepancies between the various sets of experimental data, there has existed considerable uncertainty of the value of the ion mobility. In addition, the nature of the ion involved has been controversial, primarily as a result of the lack of suitable theoretical values with which to compare with experiment. The present studies were undertaken in an attempt to obtain reliable measurements of the ion mobilities in the major energy range of interest, i.e., at low values of the electric field to pressure ratio. In addition these studies were undertaken in order to obtain information concerning the temperature variation of the mobilities, and if possible to shed some light on the ionic species involved.

## APPARATUS

The mobility tube used in the present studies has been described in detail previously[1]; therefore, only a brief description will be given here. The tube, which is shown schematically in Fig. 1, consists of a shielded discharge region in which a short-duration pulse is generated, a grid which admits the ions to the drift region, and a collector electrode to which the ions drift under the influence of an applied electric field. The motion of the ions in the drift region induces a current in a resistor in the external circuit. Following amplification, the resulting voltage waveform is applied to a synchroscope with a calibrated time base. The ion transit times are determined from the breaks in the waveforms which occur when the ions reach the collector.

As in previous studies[2] of the variation of the mobility with temperature, the mobility tube is immersed in a refrigerating bath either at 77°K (liquid nitrogen) or at 195°K (dry ice). The refrigerants are contained in a styrofoam chamber which surrounds the tube. In the low-temperature measurements several hours were permitted to elapse, before taking the measurements following the introduction of the gas into the tube, in order to allow the tube and the gas to achieve thermal equilibrium at the refrigerant temperature.

The gas samples used in these studies are introduced to the mobility tube by means of an ultra-high vacuum gas handling system.[3] Following extended bakeout at

[1] M. A. Biondi and L. M. Chanin, Phys. Rev. **94**, 910 (1954).

[2] L. M. Chanin and M. A. Biondi, Phys. Rev. **106**, 473 (1957).

[3] D. Alpert, J. Appl. Phys. **24**, 860 (1953).