

A FORTRAN PROGRAM FOR CALCULATING THE MEANSQUARE VALUES OF THE ELECTRON MOMENTA IN N-ELECTRON ATOMS He-Kr

LEE WEI MING

*Instructor, Collage of Engineering, National Chiao Tung University,
Hsinchu, Taiwan, Republic of China*

(Received 4 December 1973)

Abstract: *The one-electron part of the total mean square values of electron momenta in N-electron atoms can be expressed as $\langle \psi | \sum_{i=1}^N P_i^2 | \psi \rangle$. The total wave function ψ is a linear combination of spin-orbitals ϕ . ϕ is expanded in terms of Slater type orbital (STO). In this paper, a Fortran program was designed to solve this lengthy calculation.*

1. INTRODUCTION

Owing to the interelectronic repulsions, the Schroedinger equation for the N-electron atom could not be separated into n one-electron hydrogen-like equations. The Hamiltonian does not contain spin terms so that the energy is unaffected by the inclusion of the spin factor. The fundamental particles, electrons, neutrons, and protons, are all antisymmetric and are known as Fermi-Dirac particles or "fermions". According to the Pauli principle¹, the over-all wavefunction including spin must be antisymmetric with respect to interchange of the two electrons. Slater determinants of spin-orbital provide the proper antisymmetrization. The total ground state Hartree-Fock wavefunction of N-electron atoms with closed shell is²

$$\psi_{total} = \frac{1}{\sqrt{N!}} |\phi_1(1)\phi_2(2)\phi_3(3)\dots\phi_N(N)| \quad (1)$$

Slater orbitals³ are often used to give a simple approximate representation of atomic orbitals. In Clementi's analytical Hartree-Fock functions the orbital wave function ϕ_{nlm} is expanded in terms of Slater type orbital X_{jl} ³, i. e.

$$\phi_{nlm} = R_{nl}(r) Y_m^l(\theta, \phi) \quad (2)$$

$$R_{nl}(r) = \sum_j C_{jl} X_{jl} \quad (3)$$

$$X_{jl} = N_{jl} r^n j l^{-1} \exp(-\rho_{jl} \cdot r) \quad (4)$$

$$N_{jl} = [(2\rho_{jl})^{2n} j l^{+1} / (2n_{jl}!)]^{1/2} \quad (5)$$

where C is the STO expansion coefficients, ρ is the orbital exponent, j is an index for the basis set of STO, n is an integer, and l is the azimuthal quantum number of STO. Take the atom of He(1S) for example,

STO Is orbital	Orbital Exponent of Is orbital	Expansion Coefficient of Is orbital
X_{10}	$\rho_{10}=1.4300$	$C_{10}=0.78503$
X_{20}	$\rho_{20}=2.4415$	$C_{20}=0.20284$
X_{30}	$\rho_{30}=4.0996$	$C_{30}=0.03693$
X_{40}	$\rho_{40}=6.4843$	$C_{40}=-.00293$
X_{50}	$\rho_{50}=6.7978$	$C_{50}=0.00325$

thus, the orbital wave function ϕ_{1s} of the atom He is given by the equation,

$$\phi_{1s} = 0.78503X_{10} + 0.20284X_{20} + 0.03693X_{30} - 0.00293X_{40} + 0.0325X_{50} \quad (6)$$

2. FORM OF THE FORTRAN PROGRAM

Based on the Clementi's analytical Hartree-Fock function, the equation which shows the one-electron part of the total mean square values of electron momenta between STO orbitals, *i.e.*, M orbital and K orbital, in N -electron atoms can be expressed⁴ as

$$\begin{aligned} & \langle \psi | \sum_{i=1}^N p_i^2 | \psi \rangle \\ &= - \left(\frac{\hbar}{2\pi} \right)^2 \sum_{i=1}^N C_{ji}^M C_{ji}^K \left[\frac{(2\rho_M)^{2n_M+1} (2\rho_K)^{2n_K+1}}{(2n_M)! (2n_K)!} \right]^{1/2} \\ & \times \left[\frac{n_M + n_K - 2}{(\rho_M + \rho_K)^{n_M + n_K + 1}} \right] \{ (n_K(n_K - 1) - l(l + 1) (\rho_M + \rho_K)^2 \\ & - 2n_K(n_M + n_K - 1)\rho_M(\rho_M + \rho_K) + (\rho_M + \rho_K)(n_M + n_K - 1)(\rho_K)^2) \} \end{aligned} \quad (7)$$

where \hbar is Plank's constant.

The Fortran program was designed as the following form,

```

C THIS PROGRAM CALCULATES (NL/P**2) FOR THE ATOMS K-KR.
C N IS THE NUMBER OF STO IN THE EXPANSION OF AN ORBITAL.
C LAST IS 1 IF MORE SET OF ORBITALS FOLLOW THE SET BEING.
C WORKED ON EITHER IN THE SAME ATOM OR INA NEW ATOM.
C LOST IS 1 FOR THE LAST ORBITAL SET FOR A GIVEN ATOM. OTHERWISE
IT IS 0
C LEST IS 1 IF THE NEXT ORBITAL HAS THE SAME L VALUE AS THE ONE
BEING WORKED ON. OTHERWISE IT IS 0.
C C IS THE STO EXPANSION COEFFICIENT.
C NA IS THE STO N.
C ZETA IS THE STO ORBITAL EXPONENT.
C B IS THE NAME OF THE ATOM.
C NUMB IS THE NUMBER OF ELECTRONS IN THE SHELL.
C LANG IS THE AZIMUTHAL QUANTUM NUMBER OF STO.
DIMENSION C(11), ZETA(11), NA(11), ANA(11)
DIMENSION A(9), B(24)
WRITE(5,201)
    
```

```

201 FORMAT(96H1.....1S.....2S.....3S.....4S.....2P.....3P.....4P.....3D.....TOTAL...)
    READ(2,300)B
300 FORMAT(A6)
    LINE=1
    PTOT=0.0
    DO 51 J=1,9
51 A(J)=0.0
    INDEX=1
16 READ(2,100)N, LAST, LOST
    DO 10 J=1,N
10 READ(2,101)ZETA(J),NA(J)
14 READ(2,104)LANG,LEST,NUMB
    DO 11 J=1,N
11 READ(2,102)C(J)
    PSUM=0.0
    DO 12 M=1,N
    DO 12 K=1,N
    L1=2*NA(M)
    L2=2*NA(K)
    L3=NA(M)+NA(K)-2
    XF1=1.
    XF2=1.
    XF3=1.
    DO I=1,L1
    F=I
20 XF1=XF1*F
    DO 21 I=1,L2
    F=I
21 XF2=XF2*F
    DO 22 I=1,L3
    F=I
22 XF3=XF3*F
    ANA(M)=NA(M)
    ANA(K)=NA(K)
    ALANG=LANG
    S4=((2.*ZETA(M))**(2*NA(M)+1))*(2.*ZETA(K))**(2*NA(K)+1)
    S5=(ZETA(M)+ZETA(K))**(NA(M)+NA(K)+1)
    S6=(ANA(K)*(ANA(K)-1.)-ALANG*(ALANG+1)*(ZETA(M)+ZETA(K)))**2
    S7=2.*ANA(K)*(ANA(M)+ANA(K)-1.)*ZETA(K)*(ZETA(M)+ZETA(K))
    S8=(ANA(M)+ANA(K))*(ANA(M)+ANA(K)-1.)*ZETA(K)**2
    FACT=C(M)*C(K)*SQRT(S4/(XF1*XF2))*(XF3/S5)
    FACT=FACT-(S6-S7+S8)

```

```

12 PSUM=PSUM-FACT
   IF(LANG-2)30,31,30
31 INDEX=8
30 A(INDEX)=PSUM
   INDEX=INDEX 1
   ANUMB=NUMB
   PTOT=PTOT+ANUMB*PSUM
   IF(LEST-1)13,14,13
13 CONTINUE
   IF(LOST-1)17,18,17
18 A(9)=PTOT
   WRITE(5,202)A,B(LINE)
   LINE=LINE+1
   PTOT=0.0
   INDEX=1
17 IF(LAST-1)15,16,15
15 CONTINUE
100 FORMAT(F10.5,15)
102 FORMAT(F10.5)
104 FORMAT(3I5)
202 FORMAT(5X,8F10.5,F11.5,3X,A6)
   CALL EXIT
   END

```

3. RESULT AND DISCUSSION

The results of the calculations are given in Appendix. All calculations were done in extended precision on an IBM 1130 computer. Atomic units are used throughout. According to the Virial theorem⁵, $\langle \psi | \sum_{i=1}^N p_i^2 | \psi \rangle$ equal to $-2 \sum_{i=1}^N (I.P.)_i$, where $I.P.$ is ionization potential⁶. The results show that there is about 1% difference between the two. The differences are due to two reasons. The first one is that a Hartree-Fock wavefunction takes into account the interactions between electrons only in an average way⁷. The second reason is that we take the mass of electron equal to unity. Actually, there is a relativistic change of electron mass with velocity in the high kinetic inner-shell electrons.

APPENDIX

Comparison between the total ionization potential(I.P.) of the atoms
He-Ca and the mean square values of electron momenta(He-Kr)

Atom	$\langle \sum_{i=1}^N P_i^2 \rangle$	$2\sum_{i=1}^N (I.P.)_i$	Atom	$\langle \sum_{i=1}^N P_i^2 \rangle$	$2\sum_{i=1}^N (I.P.)_i$
He 1S	5.72355	5.82616	Cl 2P	918.94697	925.84718
Li 2S	14.86553	15.00596	Ak 1S	1053.53119	1061.76342
Be 1S	29.14530	29.43502	K 2S	1198.31715	1207.96131
B 2P	49.05820	49.48134	Ca 1S	1353.51724	1364.75774
C 3P	75.37582	75.96460	Sc 2D	1519.46474	
C 1D	75.26215		Ti 3F	1696.81972	
C 1S	75.10167		V 4F	1885.79406	
N 4S	108.80208	109.58914	Cr 5D	2086.62718	
N 2D	108.59444		Mn 6S	2299.69508	
N 2P	108.45700		Fe 5D	2524.84321	
O 3P	149.61954	150.72226	Co 4F	2762.78064	
O 1D	149.45555		Ni 3F	3013.73775	
O 1S	149.22081		Cu 2S	3277.95530	
F 2P	198.81721	200.27986	Cu 2D	3277.88794	
Ne 1S	257.09157	258.96364	Zn 1S	3555.69808	
Na 2S	323.69289	325.94284	Ga 2P	3846.49180	
Mg 1S	399.20982	401.95862	Ge 3P	4150.66742	
Al 2P	483.72157	487.04748	Ge 1D	4150.63301	
Si 3P	577.66689	581.67500	As 4S	4468.45253	
Si 1D	577.60983		As 2D	4468.32700	
Si 1S	577.52556		As 2P	4468.23827	
P 4S	681.40003	686.18060	Se 3P	4799.73325	
P 2D	681.25451		Se 1D	4799.58950	
P 2P	681.17923		Se 1S	4799.50887	
S 3P	794.96768	800.73996	Br 2P	5144.89122	
S 1D	794.86750		Kr 1R	5504.07013	
S 1S	794.71901				

REFERENCES

1. I.N. Levine, "Quantum Chemistry" Vol. I, (Allyne and Bacon, Inc., Boston) pp. 260-263, 1970.
2. Ref. 1, p. 274.
3. E. Clementi, IBM J. Res. Develop. 9, 2 (1965). Supplement, "Table of Atomic Functions".
4. Wei-Ming Lee, "Oscillator Strength Sums S (1), S (2) and Average Dispersion Coefficients C_o: He to Kr". (Unpublished)
5. J.C. Slater, "Quantum Theory of Atomic Structure", Vol. I (Mc-Graw-Hill Book Company, New York, 1960), p. 315.
6. C.E. Moore, "Ionization Potential and Ionization Limit Derived from the Analysis of Optical Spectra" NSRDS-NBS 34, Washington D.C., 1970.
7. Ref. 1, pp. 280-286.