Properties of single-term atomic states calculated in a variationally optimized-local-central-potential model

K. Aashamar*
Department of Physics and Center for Chemical Physics, University of Western Ontario, London, Ontario N6A 3K7, Canada

T. M. Luke and J. D. Talman
Departments of Applied Mathematics and Physics and Center for Chemical Physics, University of Western Ontario, London, Ontario N6A 5B9, Canada

(Received 23 June 1978)

A method has been developed for calculating properties of single-term atomic states using a variationally optimized effective local central potential. The method has been applied to the ground states and, in certain cases, low-lying excited states of the elements with $3 \leq Z \leq 54$. Results are presented for the energies of these states and certain other properties such as dipole polarizabilities and single-particle orbital parameters. The results show that the method leads to wave functions that are very close to Hartree-Fock wave functions but for which the single-particle orbitals can be obtained from a single numerical central potential.

I. INTRODUCTION

The Hartree-Fock (HF) approximation[1] can be applied to atoms in a variety of ways because of the fact that a single Slater determinant composed of single-particle angular-momentum eigenfunctions is in many cases not an eigenfunction of the total orbital and spin angular momenta.

For an open-shell atom such as carbon, one approach, which we will call single-term Hartree-Fock (STHF), is to form an eigenfunction, e.g., ^3P, of the L^2 and S^2 operators from the ground-state $(1s)^2(2s)^2(2p)^2$ configuration, and carry out the variational calculation for the expectation value of the Hamiltonian with respect to the single-particle orbitals. Another approach, which we will call configuration-averaged Hartree-Fock (CAHF) is to average (with the statistical weights) the expectation value of H over all the terms of the ground-state configuration before performing the variational calculation. This method, which has been called "hyper-HF" by Slater[2] is somewhat simpler to implement than STHF, because the averaging process is essentially an angle averaging, and eliminates the angular dependence from the problem in a simple way.

Complete results for the ground or close-to-ground states of all atoms in STHF have been given by Froese Fischer,[1] and similar results for CAHF have been given by Mann.[3] For closed-shell atoms or atoms with one valence electron or one hole in a closed shell, the two methods are the same.

In a previous article,[4] (hereafter referred to as I) a variationally optimized effective central potential model for atoms has been developed. This model used the configuration-averaged expectation value for H. This method will be called the configuration-averaged optimized-potential model (CAOPM). It has been found[4-6] that this method gives results that are in very close agreement with the corresponding CAHF results.

In this article, the methods of I will be extended to develop an effective potential model for the case in which the expectation value of H is calculated for a single term. Because of the success of the CAOPM in approximating the CAHF results, it was felt that this would lead to results close to the STHF results.

The theory for the model will be developed in Sec. II and some of the numerical details discussed in Sec. III. The results for a selection of properties of certain atoms will be given in Sec. IV and compared with the STHF and CAOPM results. It is found that the results are again very close to the Hartree-Fock results. The effective potentials are in most cases rather close to the potentials found in the CAOPM calculations. We also have presented results for the ground-state configurations of certain transition elements for which numerical HF results do not seem to be readily available.

II. THEORY

We consider a single wave function of the form

$$\Psi(LS)=\sum C_{LS}(m_1,m_2,\ldots,m_N)|m_1,m_2,\ldots,m\rangle\,, \tag{2.1}$$

where $|m_1,m_2,\ldots,m_N\rangle$ represents a Slater determinant with orbitals of magnetic quantum numbers $m_1,m_2,\ldots,m_N$ occupied. The n and l quantum numbers are omitted for convenience. The quantity $\langle\Psi(LS)|H|\Psi(LS)\rangle$ can be expressed in the form (in units in which $\frac{1}{2}e^2=\hbar=2m=1$)

$$\langle H\rangle=\sum_i q_i I(i,i)+\sum_{ijkl\lambda} b_{ijkl}(\lambda)R_\lambda(ijkl), \tag{2.2}$$

where

$$I(i,i)=\int_0^\infty P_i(r)\left(-\frac{d^2}{dr^2}+\frac{l_i(l_i+1)}{r^2}-\frac{2Z}{r}\right)P_i(r)\,dr, \tag{2.3}$$

$$R_\lambda(ijkl)=2\int_0^\infty dr\int_0^\infty dr' P_i(r)P_j(r') \times(r_<^\lambda/r_>^{\lambda+1})P_k(r)P_l(r'). \tag{2.4}$$

In the present one-term calculation, only the terms $(kl)=(ij)$ or $(kl)=(ji)$ occur in the two-particle terms in Eq. (2.2). The coefficients q_i and $b_{ijkl}(\lambda)$ are purely geometric, and are calculated from the $C_{LS}(m_1, m_2, \ldots, m_N)$ of Eq. (2.1) for the particular term of interest. The functions $P_i(r)$ are the reduced radial-wave functions for the single-particle orbitals. In the present calculation they are assumed to satisfy the reduced radial Schrödinger equation

$$-\frac{d^2P_i}{dr^2}+\frac{l_i(l_i+1)}{r^2}P_i-\frac{2Z}{r}P_i+V(r)P_i=e_iP_i, \tag{2.5}$$

where $V(r)$ is the effective central potential that is to be varied.

The variational problem is to minimize $\langle H\rangle$ subject to variations in $V(r)$. This requires that

$$\frac{\delta\langle H\rangle}{\delta V(r)}=\sum_i\int_0^\infty\frac{\delta\langle H\rangle}{\delta P_i(r')}\frac{\delta P_i(r')}{\delta V(r)}\,dr'=0. \tag{2.6}$$

It is seen that

$$\begin{aligned}\frac{\delta\langle H\rangle}{\delta P_i(r)}&=2q_i\left(-\frac{d^2}{dr^2}+\frac{l_i(l_i+1)}{r^2}-\frac{2Z}{r}\right)P_i(r)\\&\quad+4\sum_k U_{ik}(r)P_k(r)\\&=2q_i[e_i-V(r)]P_i(r)\\&\quad+4\sum_k U_{ik}(r)P_k(r),\end{aligned} \tag{2.7}$$

where

$$U_{ik}(r)=2\sum_{jl\lambda}b_{ijkl}(\lambda)\int_0^\infty dr' P_j(r')(r_<^\lambda/r_>^{\lambda+1})P_l(r'). \tag{2.8}$$

It was shown in I that

$$\frac{\delta P_i(r')}{\delta V(r)}=-G_i(r,r')P_i(r), \tag{2.9}$$

where $G_i(r,r')$ is the Green's function for the reduced radial equation

$$G_i(r,r')=\sum_{k\neq i}(e_k-e_i)^{-1}P_k(r)P_k(r'). \tag{2.10}$$

An explicit expression for $G_i(r,r')$ has been given in I.

When Eqs. (2.7) and (2.9) are combined with (2.6), it is found that the effective potential $V(r)$ satisfies the integral equation

$$\int_0^\infty H(r,r')V(r')\,dr'=Q(r), \tag{2.11}$$

where

$$H(r,r')=\sum_i q_iP_i(r)G_i(r,r')P_i(r'), \tag{2.12}$$

$$Q(r)=2\sum_{ik}\int dr' P_i(r)G_i(r,r')U_{ik}(r')P_k(r'). \tag{2.13}$$

In deriving (2.11), the terms in e_i in Eq. (2.7) have dropped out because the Green's function $G_i(r,r')$ is orthogonal to $P_i(r)$. The variational problem has now been reduced to the problem of obtaining self-consistent solutions to Eqs. (2.5) and (2.11).

III. NUMERICAL METHODS

Equations (2.5) and (2.11) have been solved numerically in logarithmic variables $\rho=\ln r$, $-8.0<\rho<4.6$. The differential equation (2.5) has been solved using the Numerov method with various values of $\Delta\rho$ with the integration being cut off when $P_i(r)\sim10^{-5}$. The integral equation (2.11) is solved by replacing the integral by a summation and treating the equation as a system of linear equations. For this part of the calculation $\Delta\rho$ was 0.2.

The solution of Eq. (2.11) has a potential difficulty in that the kernel is singular since $V(r)=1$ is a solution of the homogeneous problem. In practice, the integral is cut off at a suitable $r\sim10a_0$, and the potential is extrapolated as a Coulomb potential for larger r. It was shown in I that for the COAPM the potential behaves like the static potential produced by the atom with one electron removed for large r. It can be proved that this is also the case in the present calculation. The calculated $V(r)$, which can contain an arbitrary additive constant, has been matched to this asymptotic behavior at $r_{\max}$.

The atomic-structure program of Eissner and Nussbaumer[7] has been used for the calculation of the geometric coefficients q_i and $b_{ijkl}(\lambda)$. After the optimized effective potential was obtained, the total energy calculation was performed using this program.

IV. RESULTS

The numerical results of the present calculation are presented in Tables I and II. The results can be compared with the numerical HF results of

TABLE I. Comparison of ground-state (and some near-ground-state) total energies and polarizabilities for the neutral atoms from Li through Xe. Except for entries labelled by a letter, the HF energies are those of Ref. 1, and the HF polarizabilities those of Ref. 8.

		Energy (Ry)		ΔE	Polarizability (Å^3)		
Element	Term	OPM	HF	ppm	OPM	HF	Exp.
3 Li	$2s\,^2S$	− 14.8648	− 14.8655	47	15.96	15.96	22 ±2 [b]
4 Be	$(2s)^2\,^1S$	− 29.1448	− 29.1460	41	7.81	7.77	
5 B	$2p\,^2P$	− 49.0555	− 49.0581	53	3.48	3.43	
6 C	$(2p)^2\,^3P$	− 75.3730	− 75.3772	56	1.78	1.74	
7 N	$(2p)^3\,^4S$	− 108.7964	− 108.8019	51	1.03	1.00	1.13 ± 0.06 [c]
8 O	$(2p)^4\,^3P$	− 149.6149	− 149.6188	26	0.75	0.73	0.77 ± 0.06 [c]
9 F	$(2p)^5\,^2P$	− 198.8157	− 198.8187	15	0.54	0.53	
10 Ne	$(2p)^6\,^1S$	− 257.0910	− 257.0942	11	0.40	0.39	0.3946 [b]
11 Na	$3s\,^2S$	− 323.7119	− 323.7178	18	18.74	18.67	21.5 ±2 [d]
							24.4 ±1.7 [b]
12 Mg	$(3s)^2\,^1S$	− 399.2223	− 399.2293	18	14.26	14.13	$\begin{cases}7.0\\7.4\end{cases}$ ±1.8 [e]
13 Al	$3p\,^2P$	− 483.7462	− 483.7534	15	11.18	10.97	
14 Si	$(3p)^2\,^3P$	− 577.7008	− 577.7087	14	6.98	6.81	
15 P	$(3p)^3\,^4S$	− 681.4264	− 681.4376	16	4.55	4.42	
16 S	$(3p)^4\,^3P$	− 794.9998	− 795.0098	13	3.53	3.44	
17 Cl	$(3p)^5\,^2P$	− 918.9569	− 918.9641	9	2.67	2.61	
18 Ar	$(3p)^6\,^1S$	−1 053.623	−1 053.635	11	2.02	1.98	1.641 ± 0.002 [b]
19 K	$4s\,^2S$	−1 198.314	−1 198.330	13	37.69	37.58	45.7 ± 6 [f]
							45.2 ±3.2 [b]
20 Ca	$(4s)^2\,^1S$	−1 353.503	−1 353.516	10	33.91	33.80	$\begin{cases}19.7\\22.5\end{cases}$ ± 0.6 [e]
21 Sc	$3d(4s)^2\,^2D$	−1 519.452	−1 519.471	13	25.59	26.80	
22 Ti	$(3d)^2(4s)^2\,^3F$	−1 696.789	−1 696.812	14	21.85	22.40	
23 V	$(3d)^3(4s)^2\,^4F$	−1 885.740	−1 885.769	15	19.03	19.10	
24 Cr	$(3d)^5 4s\,^7S$	−2 086.687	−2 086.710 [a]	11	9.97	11.5 [g]	
			2086.714 [h]	11			
	$(3d)^4(4s)^2\,^5D$	−2 086.588	−2 086.620	15	15.92	16.60	
			−2 086.619 [a]	15			
25 Mn	$(3d)^5(4s)^2\,^6S$	−2 299.692	−2 299.732	17	14.70	14.60	
26 Fe	$(3d)^6(4s)^2\,^5D$	−2 524.854	−2 524.887	13	12.93	12.70	
27 Co	$(3d)^7(4s)^2\,^4F$	−2 762.791	−2 762.829	14	11.32	11.30	
28 Ni	$(3d)^8(4s)^2\,^3F$	−3 013.705	−3 013.742	12	10.13	10.20	26 ± 5 [b]
29 Cu	$(3d)^{10} 4s\,^2S$	−3 277.875	−3 277.926 [a]	16	4.86	7.32	22 ± 4 [b]
			−3277.930 [h]	17			
	$(3d)^9(4s)^2\,^2D$	−3 277.866	−3 277.900	10	8.69	9.04	
			−3 277.899 [a]	10			
30 Zn	$(3d)^{10}(4s)^2\,^1S$	−3 555.665	−3 555.696	9	8.35	8.12	
31 Ga	$4p\,^2P$	−3 846.495	−3 846.522	7	9.80	9.43	
32 Ge	$(4p)^2\,^3P$	−4 150.697	−4 150.719	5	7.28	7.01	
33 As	$(4p)^3\,^4S$	−4 468.457	−4 468.477	4	5.42	5.22	
34 Se	$(4p)^4\,^3P$	−4 799.722	−4 799.735	3	5.04	4.56	
35 Br	$(4p)^5\,^2P$	−5 144.860	−5 144.883	4	3.96	3.80	
36 Kr	$(4p)^6\,^1S$	−5 504.082	−5 504.110	5	3.25	3.12	2.48 [b]
37 Rb	$5s\,^2S$	−5 876.684	−5 876.715	5	46.14	45.96	48.7 ± 3.4 [b]
38 Sr	$(5s)^2\,^1S$	−6 263.063	−6 263.091	4	45.22	44.92	$\begin{cases}24.0\\31.4\end{cases}$ ± 0.8 [e]
							25 ± 3 [b]
39 Y	$4d(5s)^2\,^2D$	−6 663.295	−6 663.368	11	21.79	35.52	
40 Zr	$(4d)^2(5s)^2\,^3F$	−7 077.969	−7 077.990	3	26.06	29.30	
41 Nb	$(4d)^4 5s\,^6D$	−7 507.168	−7 507.169 [a]	0.1	16.79		
			−7507.198 [h]	4			
	$(4d)^3(5s)^2\,^4F$	−7 507.075	−7 507.104	4	23.20	24.92	
			−7 507.079 [a]	0.5			
42 Mo	$(4d)^5 5s\,^7S$	−7 951.078	− 7 951.068 [a]	−1	12.42	13.4 [h]	9 ± 2 [b]
			−7951.102 [h]	3			

TABLE I. *(Continued)*

		Energy (Ry)		ΔE	Polarizability (Å^3)		
Element	Term	OPM	HF	ppm	OPM	HF	Exp.
	$(4d)^4(5s)^2\ {}^5D$	−7 950.864	−7 950.887	3	20.25	21.63	
			−7 950.856 [a]	−1			
43 Tc	$(4d)^5(5s)^2\ {}^6S$	−8 409.546	−8 409.577	4	18.21	19.13	
44 Ru	$(4d)^7\ 5s\ {}^5F$	−8 883.055	−8 883.053 [a]	−0.2	10.82		
			−8883.080 [h]	3			
	$(4d)^6(5s)^2\ {}^5D$	−8 882.945	−8 882.975	3	16.51	16.88	
			−8 882.949 [a]	0.5			
45 Rh	$(4d)^8 5s\ {}^4F$	−9 371.731	−9 371.767 [a]	4	10.32		
			−9371.767 [h]	4			
	$(4d)^7(5s)^2\ {}^4F$	−9 371.574	−9 371.602	3	14.70	15.10	
			−9 371.578 [a]	0.4			
46 Pd	$(4d)^{10}\ {}^1S$	−9 875.802	−9 875.814 [a]	1	3.51	3.43	
			−9875.848 [h]	5			
	$(4d)^8(5s)^2\ {}^3F$	−9 875.520	−9 875.566	5	13.54	13.64	
			−9 875.542 [a]	2			
47 Ag	$(4d)^{10} 5s\ {}^2S$	−10 395.337	−10 395.370 [a]	3	8.59	9.59	
			−10395.398 [h]	6			
	$(4d)^9(5s)^2\ {}^2D$	−10 394.978	−10 395.036	6	12.05	12.42	
			−10 395.006 [a]	3			
48 Cd	$(5s)^2\ {}^1S$	−10 930.198	−10 930.266	6	11.07	11.41	
49 In	$5p\ {}^2P$	−11480.262	−11480.338	7	12.64	12.77	
50 Sn	$(5p)^2\ {}^3P$	−12 045.856	−12 045.863	1	8.73	10.20	
51 Sb	$(5p)^3\ {}^4S$	−12 626.914	−12 626.971	5	8.42	8.06	
52 Te	$(5p)^4\ {}^3P$	−13 223.522	−13 223.568	3	7.59	7.30	
53 I	$(5p)^5\ {}^2P$	−13 835.930	−13 835.962	2	6.62	6.31	
54 Xe	$(5p)^6\ {}^1S$	−14 464.235	−14 464.277	3	5.64	5.38	4.044 [b]

[a] Ref. 10.

[b] R. R. Teachout and R. T. Pack, At. Data 3, 195 (1971).

[c] R. A. Alpher and D. R. White, Phys. Fluids 2, 153 (1959).

[d] G. E. Chamberlain and J. C. Zorn, Phys. Rev. 129, 677 (1963).

[e] P. L. Altick, J. Chem. Phys. 40, 283 (1964).

[f] W. D. Hall and J. C. Zorn, Bull. Am. Phys. Soc. 12, 131 (1967).

[g] Ref. 9.

[h] Ref. 8.

Froese Fischer[1] and Fraga *et al.*,[8,9] the analytic wave-function HF calculations of Clementi and Roetti,[10] and where possible, with experiment. It is seen that there is general close consistency among the results, with some exceptions that will be noted in the following.

The total atomic energies and dipole polarizabilities are given in Table I for the elements Li to Xe. There are two entries for Cu, Ag, and some of the transition elements. The tables of Froese Fischer give results only for the terms in which the 4*s* (or 5*s*) shell is filled while for these elements the *s* shell is open or unoccupied in the ground state. The comparative HF results for the these true ground state terms are those of Clementi and Roetti and those of Fraga *et al.* Otherwise the Froese Fischer results are used for comparison.

Generally, the discrepancy (ΔE) in total energy from the HF results decreases from about 50 ppm for the lightest elements to about 5 ppm for the heaviest elements. We note that the agreement with the ground-state energies calculated by Clementi and Roetti is unexpectedly good, and that in two cases, Ru and Mo, the optimized potential model (OPM) energy is actually below the HF energy. Evidently, the Clementi and Roetti results are not absolute HF minima, either because the functional forms are not sufficiently general, or because the solutions have not been fully optimized.

The dipole polarizability of the ground state of a an atom is an important property in, for example, its behavior in collisions. The results for the polarizabilities were calculated using the variational method of Pople and Schofield[11] and Thorhallsson *et al.*[12] In this method the second-order energy shift of an atom in a uniform electric field is estimated variationally by multiplying the unperturbed wave function Φ by a factor of

TABLE II. Single orbital properties in the ground-state (and some near-ground-state) configurations for a selection of elements between Li and Xe. The HF results for configuration d^ns are those of Ref. 10; otherwise they are from Ref. 1. The negatives of the single-particle energies are shown.

			(−1)× Single-Particle Energy (Ry)		r		r^2		$\frac{1}{r}$		$\frac{1}{r^3}$	
Element	Term	Orbital	HF	OPM	HF	OPM	HF	OPM	HF	OPM	HF	OPM
5 B	$2p^2\,P$	1s	15.391	13.827	0.325 9	0.327 4	0.143 4	0.145 2	4.674	4.664	⋯	⋯
		2s	0.989 41	1.057 0	1.977	1.957	4.709	4.596	0.7129	0.7260	⋯	⋯
		2p	0.619 71	0.620 32	2.205	2.254	6.146	6.432	0.6050	0.5966	0.7756	0.7907
			(0.610)									
10 Ne	$2p^6\ {}^1S$	1s	65.545	61.631	0.157 6	0.157 9	0.033 47	0.033 62	9.618	9.613	⋯	⋯
		2s	3.860 8	3.4255	0.892 1	0.894 8	0.967 1	0.973 0	1.633	1.630	⋯	⋯
		2p	1.700 8	1.6926	0.965 3	0.966 1	1.228	1.232	1.435	1.436	10.91	11.04
			(1.585)									
14 Si	$3p^2\ {}^3P$	1s	137.62	131.31	0.111 4	0.111 5	0.016 70	0.016 73	13.58	13.58	⋯	⋯
		2s	12.313	10.684	0.562 9	0.566 7	0.377 3	0.383 1	2.590	2.574	⋯	⋯
		2p	8.512 1	7.4413	0.535 4	0.536 2	0.359 7	0.361 5	2.456	2.457	47.27	47.57
		3s	1.079 7	1.0825	2.207	2.190	5.676	5.578	0.6032	0.6142	⋯	⋯
		3p	0.594 23	0.596 15	2.752	2.774	8.981	9.136	0.4780	0.4787	2.054	2.203
			(0.599)									
17 Cl	$3s^23p^5\ {}^2P$	1s	209.77	201.92	0.091 30	0.091 33	0.011 20	0.011 21	16.56	16.56	⋯	⋯
		2s	21.215	19.026	0.441 7	0.444 2	0.231 2	0.234 1	3.314	3.296	⋯	⋯
		2p	16.144	14.594	0.405 7	0.406 3	0.204 3	0.205 3	3.202	3.200	100.4	100.7
		3s	2.145 8	1.8818	1.556	1.550	2.813	2.794	0.8749	0.8855	⋯	⋯
		3p	1.012 8	1.0054	1.842	1.848	4.059	4.090	0.7333	0.7354	6.769	7.059
			(0.956)									
24 Cr	$3d^44s^2\ {}^5D$	1s	441.18	429.50	0.064 15	0.064 16	0.005 52	0.005 52	23.53	23.53	⋯	⋯
		2s	52.878	49.152	0.294 0	0.295 2	0.102 0	0.102 8	5.013	4.99	⋯	⋯
		2p	44.731	41.815	0.260 1	0.260 6	0.083 06	0.083 43	4.931	4.926	350.5	350.6
		3s	6.998 2	5.944 4	0.905 1	0.907 5	0.943 2	0.948 4	1.542	1.543	⋯	⋯
		3p	4.497 7	3.901 5	0.965 6	0.961 9	1.097	1.087	1.410	1.418	39.65	40.85
		3d	1.138 3	0.717 10	1.219	1.245	1.910	2.038	1.083	1.077	3.348	3.385
		4s	0.479 48	0.477 36	3.494	3.391	14.17	13.55	0.3643	0.3900	⋯	⋯
	$3d^54s\ {}^7S$ (ground)	1s	440.77	428.99		0.064 16		0.005 52		23.53		⋯
		2s	52.419	48.580		0.295 5		0.103 1		4.987		⋯
		2p	44.279	41.250		0.260 8		0.083 60		4.924		350.5
		3s	6.569 9	5.648 9		0.914 4		0.964 6		1.532		⋯
		3p	4.101 4	3.620 7		0.974 9		1.120		1.402		39.91
		3d	0.746 96	0.495 98		1.404		2.720		0.9964		2.911
		4s	0.443 88	0.466 92		3.478		14.20		0.3773		⋯
			(.497)									
29 Cu	$3d^9\,4s^2\ {}^2D$	1s	658.07	643.65	0.052 88	0.052 87	0.003 75	0.003 75	28.51	28.52	⋯	⋯
		2s	82.169	77.298	0.237 5	0.238 2	0.066 50	0.066 87	6.225	6.202	⋯	⋯
		2p	71.758	67.786	0.207 5	0.207 7	0.052 75	0.052 81	6.157	6.156	672.3	673.2

TABLE II. *(Continued)*

			(−1)× Single Particle Energy (Ry)		r		r^2		$\frac{1}{r}$		$\frac{1}{r^3}$	
Element	Term	Orbital	HF	OPM	HF	OPM	HF	OPM	HF	OPM	HF	OPM
		3*s*	10.521	8.949 1	0.718 4	0.720 8	0.595 3	0.599 2	1.959	1.955	•••	•••
		3*p*	7.113 8	5.982 5	0.751 0	0.750 7	0.665 1	0.663 9	1.824	1.825	83.02	83.76
		3*d*	1.480 4	1.048 6	0.918 3	0.925 3	1.105	1.136	1.457	1.456	8.154	8.246
		4*s*	0.569 48	0.583 76	2.973	2.896	10.37	9.965	0.4303	0.4560	•••	•••
	$3d^{10}4s\ ^2S$ (ground)	1*s*	657.58	643.47		0.052 87		0.003 75		28.53		...
		2*s*	81.636	77.008		0.238 1		0.066 81		6.207		...
		2*p*	71.234	67.518		0.207 5		0.052 74		6.159		674.1
		3*s*	10.023	8.721 7		0.722 7		0.602 9		1.951		...
		3*p*	6.648 3	5.758 8		0.754 7		0.672 1		1.817		82.94
		3*d*	0.981 48	0.851 81		0.983 3		1.327		1.406		7.743
		4*s*	0.475 90 (0.568)	0.624 61		2.953		10.26		0.4413		...
41 Nb	$4d^3 5s^2\ ^4F$	1*s*	1371.14	1350.0	0.037 19	0.037 17	0.001 85	0.001 85	40.49	40.53	•••	...
		2*s*	194.22	186.06	0.162 6	0.162 8	0.031 08	0.031 16	9.134	9.116	•••	
		2*p*	177.91	170.89	0.139 8	0.139 7	0.023 83	0.023 80	9.094	9.098	2124	2129
		3*s*	34.763	31.427	0.451 6	0.453 7	0.233 3	0.235 5	3.159	3.144	•••	...
		3*p*	28.430	25.645	0.448 3	0.449 9	0.233 5	0.235 3	3.057	3.045	346.0	343.8
		3*d*	16.923	15.099	0.430 8	0.431 6	0.222 9	0.224 0	2.857	2.855	49.98	50.07
		4*s*	5.330 7	4.417 0	1.188	1.189	1.596	1.601	1.123	1.131	•••	...
		4*p*	3.344 5	2.838 6	1.313	1.312	1.972	1.970	1.007	1.013	43.51	45.47
		4*d*	0.811 74	0.532 04	1.900	1.956	4.346	4.711	0.6948	0.6875	3.174	3.234
		5*s*	0.433 20	0.440 25	3.928	3.775	17.72	16.52	0.3199	0.3426	•••	...
	$4d^4 5s\ ^6D$ (ground)	1*s*	1370.9	1350.0		0.037 19		0.001 85		40.50		...
		2*s*	193.95	185.70		0.162 8		0.031 18		9.111		...
		2*p*	177.64	170.56		0.139 7		0.023 80		9.099		2130
		3*s*	34.489	31.188		0.453 9		0.235 8		3.143		...
		3*p*	28.158	25.411		0.450 1		0.235 5		3.045		343.8
		3*d*	16.652	14.850		0.432 1		0.2247		2.852		49.92
		4*s*	5.068 9	4.251 6		1.194		1.617		1.126		•••
		4*p*	3.108 3	2.682 9		1.324		2.011		1.006		44.77
		4*d*	0.597 52	0.439 98		2.149		5.846		0.6385		2.772
		5*s*	0.428 44 (0.498)	0.454 19		3.857		17.17		0.3321		•••
42 Mo	$4d^4 5s^2\ ^5D$	1*s*	1442.7	1421.0	0.036 30	0.036 27	0.001 76	0.001 76	41.49	41.53	•••	•••
		2*s*	206.02	197.54	0.158 4	0.158 6	0.029 50	0.029 56	9.378	9.361	•••	•••
		2*p*	189.20	181.89	0.136 1	0.136 0	0.022 57	0.022 54	9.340	9.345	2298	2304
		3*s*	37.483	33.974	0.437 6	0.439 6	0.218 9	0.221 1	3.264	3.248	•••	•••
		3*p*	30.885	27.939	0.433 3	0.435 0	0.218 0	0.219 8	3.164	3.151	380.7	378.0
		3*d*	18.877	16.900	0.413 3	0.414 4	0.204 6	0.206 1	2.970	2.967	55.77	55.77

TABLE II. *(Continued)*

		(−1) × Single Particle Energy (Ry)			r		r^2		$\frac{1}{r}$		$\frac{1}{r^3}$	
Element	Term	Orbital	HF	OPM	HF	OPM	HF	OPM	HF	OPM	HF	OPM
		4*s*	5.820 4	4.858 5	1.137	1.138	1.462	1.465	1.177	1.184	...	...
		4*p*	3.714 7	3.162 2	1.249	1.247	1.785	1.779	1.061	1.068	50.11	52.29
		4*d*	0.940 02	0.628 99	1.747	1.787	3.665	3.903	0.7558	0.7501	3.954	4.036
		5*s*	0.449 32	0.456 87	3.794	3.650	16.55	15.50	0.3317	0.3549	...	...
	$4d^55s\ ^7S$ (ground)	1*s*	1442.4	1421.1		0.036 27		0.001 76		41.53		...
		2*s*	205.71	197.40		0.158 6		0.029 57		9.359		...
		2*p*	188.89	181.75		0.136 0		0.022 55		9.344		2304
		3*s*	37.170	33.896		0.439 5		0.220 9		3.249		...
		3*p*	30.574	27.865		0.434 8		0.219 6		3.152		378.5
		3*d*	18.568	16.821		0.414 0		0.205 6		2.968		55.78
		4*s*	5.522 4	4.6925		1.143		1.479		1.181		...
		4*p*	3.444 1	3.007 7		1.258		1.815		1.060		51.52
		4*d*	0.713 66	0.538 53		1.914		4.557		0.7089		3.572
		5*s*	0.443 96	0.474 28		3.648		15.37		0.3522		...
			(0.522)									
44 Ru	$4d^65s^2\ ^5D$	1*s*	1591.3	1568.6	0.034 62	0.034 60	0.001 60	0.001 60	43.48	43.53	...	...
		2*s*	230.65	221.75	0.150 6	0.150 8	0.026 67	0.026 71	9.865	9.849	...	...
		2*p*	212.81	205.09	0.129 2	0.129 1	0.020 34	0.020 31	9.831	9.836	2674	2681
		3*s*	43.158	39.416	0.412 0	0.413 8	0.194 0	0.195 7	3.474	3.457	...	...
		3*p*	36.025	32.871	0.406 2	0.407 6	0.191 4	0.192 8	3.377	3.364	456.8	453.7
		3*d*	23.011	20.858	0.382 5	0.383 3	0.174 6	0.175 6	3.196	3.193	68.57	68.61
		4*s*	6.822 8	5.7275	1.049	1.049	1.245	1.245	1.282	1.291	...	...
		4*p*	4.483 0	3.7940	1.142	1.138	1.491	1.481	1.167	1.176	64.78	67.51
		4*d*	1.138 0	0.818 52	1.533	1.559	2.823	2.959	0.8646	0.8602	5.665	5.769
		5*s*	0.479 80	0.512 20	3.565	3.480	14.67	14.11	0.3536	0.3715	...	...
	$4d^75s\ ^5F$ (ground)	1*s*	1591.0	1568.3		0.034 60		0.001 60		43.53		...
		2*s*	230.32	221.46		0.150 8		0.026 71		9.849		...
		2*p*	212.48	204.80		0.129 1		0.020 31		9.836		2681
		3*s*	42.826	39.142		0.413 8		0.195 7		3.457		...
		3*p*	35.696	32.595		0.407 6		0.192 8		3.364		453.6
		3*d*	22.684	20.577		0.383 3		0.175 6		3.193		68.59
		4*s*	6.511 1	5.457 0		1.054		1.257		1.286		...
		4*p*	4.199 6	3.535 3		1.148		1.510		1.167		66.41
		4*d*	0.823 30	0.621 12		1.652		3.381		0.8217		5.241
		5*s*	0.443 28	0.449 45		3.573		14.93		0.3613		...
			(0.541)									
45 Rh	$4d^75s^2\ ^4F$	1*s*	1668.4	1645.4	0.033 84	0.033 82	0.001 53	0.001 53	44.48	44.53	...	...
		2*s*	243.48	234.27	0.147 0	0.147 1	0.025 40	0.025 45	10.11	10.09	...	...
		2*p*	225.12	217.13	0.126 0	0.125 9	0.019 34	0.019 31	10.08	10.08	2877	2885

TABLE II. *(Continued)*

Element	Term	(−1) × Single Particle Energy (Ry)			r		r^2		$\frac{1}{r}$		$\frac{1}{r^3}$	
		Orbital	HF	OPM	HF	OPM	HF	OPM	HF	OPM	HF	OPM
		3s	46.115	42.244	0.4003	0.4019	0.1830	0.1846	3.579	3.562	...	...
		3p	38.712	35.444	0.3939	0.3951	0.1799	0.1811	3.483	3.471	498.3	495.2
		3d	25.192	22.923	0.3689	0.3697	0.1621	0.1630	3.308	3.304	75.61	75.57
		4s	7.3370	6.0755	1.011	1.010	1.156	1.155	1.334	1.345	...	...
		4p	4.8818	4.0228	1.096	1.092	1.373	1.364	1.218	1.229	72.87	76.03
		4d	1.2227	0.83018	1.451	1.480	2.531	2.670	0.9157	0.9082	6.622	6.681
		5s	0.49422	0.47765	3.467	3.382	13.89	13.33	0.3640	0.3812	...	...
	$4d^8 5s\,^4F$ (ground)	1s	1668.1	1644.7		0.03382		0.00153		44.53		...
		2s	243.13	233.85		0.1471		0.02544		10.09		...
		2p	224.77	216.71		0.1259		0.01931		10.08		2884
		3s	45.754	41.832		0.4021		0.1848		3.561		...
		3p	38.354	35.027		0.3954		0.1814		3.469		494.4
		3d	24.837	22.503		0.3701		0.1634		3.302		75.47
		4s	7.0005	5.8541		1.015		1.167		1.337		...
		4p	4.5756	3.8137		1.101		1.389		1.218		74.56
		4d	0.90252	0.67663		1.553		2.985		0.8744		6.170
		5s	0.44080	0.45309		3.559		14.88		0.3629		...
			(0.548)									
46 Pd	$4d^8 5s^2\,^3F$	1s	1747.3	1723.4	0.03310	0.03307	0.00147	0.00146	45.48	45.53	...	...
		2s	256.66	247.15	0.1436	0.1437	0.02423	0.02426	10.35	10.34	...	...
		2p	237.78	229.50	0.1230	0.1229	0.01842	0.01839	10.32	10.33	3090	3097
		3s	49.144	45.072	0.3892	0.3909	0.1731	0.1745	3.684	3.666	...	...
		3p	41.470	38.007	0.3823	0.3836	0.1694	0.1707	3.590	3.576	542.2	538.3
		3d	27.442	24.994	0.3563	0.3572	0.1510	0.1520	3.419	3.415	83.08	83.01
		4s	7.8550	6.5450	0.9762	0.9754	1.078	1.076	1.385	1.394	...	...
		4p	5.2857	4.3726	1.054	1.051	1.270	1.262	1.269	1.279	81.48	84.60
		4d	1.3147	0.95489	1.378	1.395	2.283	2.362	0.9662	0.9624	7.661	7.766
		5s	0.50730	0.51117	3.381	3.322	13.23	12.89	0.3735	0.3883	...	...
	$4d^{10}\,^1S$ (ground)	1s	1746.6	1723.3		0.03307		0.00146		45.54		...
		2s	255.93	246.66		0.1437		0.02426		10.34		...
		2p	237.06	229.03		0.1229		0.01839		10.33		3099
		3s	48.409	44.641		0.3909		0.1746		3.666		...
		3p	40.740	37.581		0.3836		0.1707		3.576		538.5
		3d	26.718	24.552		0.3573		0.1521		3.413		82.92
		4s	7.1627	6.1569		0.9822		1.093		1.385		...
		4p	4.6488	4.0058		1.064		1.300		1.264		82.57
		4d	0.66248	0.69459		1.540		2.977		0.8923		6.659
			(0.612)									
47 Ag	$4d^9 5s^2\,^2D$	1s	1828.1	1804.0	0.03239	0.03238	0.00140	0.00140	46.48	46.49	...	...
		2s	270.77	260.40	0.1403	0.1404	0.02313	0.02317	10.60	10.58	...	...
		2p	250.17	242.27	0.1201	0.1200	0.01756	0.01752	10.57	10.58	3313	3323

TABLE II. *(Continued)*

			(−1) × Single Particle Energy (Ry)		r		r^2		$\frac{1}{r}$		$\frac{1}{r^3}$	
Element	Term	Orbital	HF	OPM	HF	OPM	HF	OPM	HF	OPM	HF	OPM
		3*s*	52.247	48.074	0.3788	0.3805	0.1639	0.1653	3.788	3.769	⋯	⋯
		3*p*	44.299	40.752	0.3714	0.3726	0.1599	0.1610	3.696	3.682	588.6	584.5
		3*d*	29.761	27.225	0.3447	0.3456	0.1411	0.1420	3.530	3.524	91.00	90.84
		4*s*	8.3777	6.9911	0.9439	0.9429	1.008	1.006	1.435	1.445	⋯	⋯
		4*p*	5.6955	4.6986	1.015	1.012	1.180	1.172	1.319	1.330	90.61	94.16
		4*d*	1.4121	1.0558	1.312	1.327	2.071	2.136	1.016	1.012	8.791	8.891
		5*s*	0.51929	0.53831	3.304	3.233	12.66	12.21	0.3824	0.3987	⋯	⋯
	$4d^{10}5s\ ^2S$	1*s*	1827.7	1803.6		0.03236		0.00140		46.54		⋯
	(ground)	2*s*	269.76	260.05		0.1404		0.02316		10.58		⋯
		2*p*	250.37	241.91		0.1200		0.01752		10.58		3323
		3*s*	51.838	47.736		0.3804		0.1652		3.770		⋯
		3*p*	43.893	40.414		0.3726		0.1610		3.682		584.4
		3*d*	29.358	26.884		0.3456		0.1420		3.524		90.82
		4*s*	8.0015	6.6890		0.9465		1.015		1.440		⋯
		4*p*	5.3522	4.4086		1.019		1.190		1.321		92.79
		4*d*	1.0733	0.82079		1.385		2.365		0.9792		8.301
		5*s*	0.43944 (0.557)	0.47209		3.444		14.00		0.3756		⋯
54 Xe	$5s^25p^6\ ^1S$	1*s*	2448.8	2420.8	0.02814	0.02811	0.00106	0.00106	53.47	53.55	⋯	⋯
		2*s*	378.68	367.46	0.1209	0.1209	0.01716	0.01717	12.31	12.30	⋯	⋯
		2*p*	355.56	345.70	0.1031	0.1030	0.01292	0.01289	12.29	12.30	5183	5194
		3*s*	80.351	75.505	0.3187	0.3196	0.1159	0.1165	4.527	4.511	⋯	⋯
		3*p*	70.443	66.304	0.3094	0.3101	0.1108	0.1113	4.445	4.431	989.9	984.0
		3*d*	52.238	49.233	0.2803	0.2809	0.09263	0.09312	4.304	4.299	160.8	160.6
		4*s*	15.713	13.848	0.7453	0.7471	0.6256	0.6293	1.843	1.845	⋯	⋯
		4*p*	12.017	10.585	0.7770	0.7787	0.6855	0.6892	1.741	1.744	189.6	192.4
		4*d*	5.5556	4.9898	0.8705	0.8726	0.8809	0.8872	1.509	1.512	24.03	24.51
		5*s*	1.8886	1.7598	1.981	1.960	4.440	4.349	0.6479	0.6613	⋯	⋯
		5*p*	0.91438 (0.891)	1.0506	2.338	2.352	6.277	6.358	0.5472	0.5471	17.83	18.69

$$1+\sum_i(\mu z_i+\nu z_i r_i).$$

The parameters μ and ν are to be determined variationally. The polarizability is then given by

$$\alpha=\tfrac{2}{3}(6A_2B_0^2-8A_1B_0B_1+6A_0B_1^2)/(9A_0A_2-8A_1^2),$$

where

$$A_k=\langle\Phi|\sum_i r_i^k|\Phi\rangle,\quad B_k=\langle\Phi|\sum_{ij} r_i^k\vec{r}_i\cdot\vec{r}_j|\Phi\rangle.$$

The results show substantial agreement with the HF results, except in the case of the ground-state term of Cu and of *Y*, where there are unaccountably large discrepancies. Available experimental results are also recorded (numbers paired together represent upper and lower bounds determined from experimental oscillator strengths). In a number of cases, the agreement with experiment is reasonably good; in some of the cases in which there is a large discrepancy, it may be that configuration mixing will change the results substantially, as occurs in the case of oscillator-strength calculations. We note also that HF results for the ground-state polarizabilities of certain of the transition elements seem not to be available.

We have recorded and compared certain individual orbital properties for a selection of elements in Table II. The elements have been chosen to be representative of the various configuration types of all the elements considered, and to include all the cases for which numerical HF calculations have not been made for the ground state. The OPM single-particle energies for inner electrons may differ from the HF values by as much as 10%, as in *B*, but more generally are in agreement to within 5%. For the outer electrons the agreement between OPM and HF energies is very close except in the transition elements.

It should be noted that the single-particle energies do not seem to have a direct or quasidirect physical significance as do the HF single-particle energies, since there does not seem to be any analog to Koopmans's theorem in the OPM. Nonetheless, we have noticed that in most cases the last OPM single-particle energy is close to the corresponding HF result and is also close to the experimental ionization potential. The latter are given in parentheses under the single-particle energies.

It is of interest to note that the greatest discrepancy between the HF and OPM single-particle energies for the outer electron occurs for the *s* and *d* levels of the transition elements. These are seen to be much closer to degeneracy in the OPM, with the energy of the *s* electron being decreased and the energy of the *d* electron being increased. This degeneracy is perhaps physically reasonable because of the known competition between the levels in filling the *d* shell in the transition elements. Spectra of the transition elements show that configurations $d^n s$ and $d^{n-1}s^2$ differ in energy by small amounts of the order of 0.1 Ry. This is perhaps further evidence that the near degeneracy is significant.

It is also interesting to observe that the OPM single-particle energies for the last electron seem to be closer to the ionization potential than are the HF energies in the transition region. The orbital radial averages exhibited in Table II again show close similarity between the HF and OPM results. Differences are very slight for the inner electrons and though, for example, in the case of $\langle r^2\rangle$ a maximum discrepancy of about 7% occurs in the outer orbital, 1% or less is more usually found.

In the cases in which the numerical HF properties for the true ground states are not tabulated, the OPM results should be reliable estimates of the HF results. The properties of the outermost electrons are most sensitive to the particular term considered; the inner-shell properties are essentially independent of the term considered.

V. CONCLUSIONS

The OPM that has been previously applied to closed-shell atoms and to configuration-averaged energies of open-shell atoms can also be applied to single terms of open-shell atoms, and as seen before, the results are very close to HF results. The method has the advantage over the HF method in that the wave functions are derivable from a single central potential that is then useful for other other calculations, e.g., calculation of single-particle excited states. Because the results are so close to the HF results, the potentials would seem to be a useful alternative to the Herman-Skillman[13] potentials, which have been extensively used in atomic-structure calculations.

The potentials found have differed only slightly from the CAOPM potentials. However, certain properties may be quite sensitive to the details of the potential. For example, the splitting between the 4*s* and 3*d* levels in Mo changes considerably between the two terms considered.

Detailed results have been presented here for neutral atoms $3\leqslant Z\leqslant 54$. In addition, optimized potentials have been obtained for the further set of elements up to radon, $Z=86$. The complete set of optimized potentials will be published separately; however, the authors will attempt to satisfy any requests they receive for the potentials for particular atoms or positive ions if they are required in advance of their publication.

Finally, the method discussed here can be generalized fairly readily to multiconfiguration calculations; this will be discussed in future publications.

ACKNOWLEDGMENT

This work was supported by the National Research Council of Canada.

---

[*] On leave from University of Oslo, Oslo, Norway.

[1] C. Froese Fischer, *The Hartree-Fock Method for Atoms* (Wiley-Interscience, New York, 1977).

[2] J. C. Slater, *The Self-Consistent Field for Molecules and Solids: Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. 4.

[3] J. B. Mann, LASL Report No. LA-3690, 1967 (unpublished).

[4] J. D. Talman and W. F. Shadwick, Phys. Rev. A 14, 36 (1976). See also R. T. Sharp and G. K. Horton, Phys. Rev. 90, 316 (1955).

[5] M. M. Pant and J. D. Talman, Phys. Rev. A (to be published).

[6] M. M. Pant and J. D. Talman, Bull. Am. Phys. Soc. 23, 286 (1978).

[7] W. Eissner and N. Nussbaumer, J. Phys. B 2, 1028 (1969).

[8] S. Fraga, J. Karwoski, and K. M. S. Saxena, *Handbook of Atomic Data* (Elsevier, Amsterdam, 1976).

[9] S. Fraga, J. Thorhallsson, and C. Fisk, Theoretical Chemistry Report No. TC-6807 (1968) (unpublished).

[10] E. Clementi and C. Roetti, At. Data Nucl. Data Tables 14, 177 (1974).

[11] J. A. Pople and P. Schofield, Philos. Mag. 2, 591 (1957).

[12] J. Thorhallsson, C. Fisk, and S. Fraga, Theoret. Chim. Acta (Berlin) 10, 388 (1968).

[13] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, 1963).