Total Energies from Numerical Self-Consistent Field Calculations*

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Total energies computed by using a Hartree, a Hartree-Fock-Slater, and a relativistic Dirac-Slater numerical self-consistent field calculation for the normal ground states of all the elements are reported. These results are discussed and compared with those from two Hartree-Fock analytical wave functions and from a nonrelativistic Thomas-Fermi approximation. The methods of calculating total energies are also presented.

INTRODUCTION

RECENTLY, several different self-consistent field calculations have been completed for a wide range of atoms, and a few total energies have been reported. The purpose of this paper is to report the total energies obtained by using three numerical calculations and to compare these results with those of three independent calculations. Also, an attempt is made to explain some of the differences.

The three numerical calculations are those of Boyd, Larson, and Waber,[1] Herman and Skillman,[2] and Liberman, Waber, and Cromer.[3] These three methods differ in that the Boyd-Larson-Waber (BLW) one is a nonrelativistic Hartree (NR-H) calculation with an exchange correction used only in the total energy, the Herman-Skillman (HS) one is a nonrelativistic Hartree-Fock-Slater (NR-HFS) calculation, while the Liberman-Waber-Cromer (LWC) one is a relativistic Dirac-Slater (R-DS) calculation. These are compared with two analytical nonrelativistic Hartree-Fock (NR-HF) results, namely those of Clementi[4] and of Watson.[5] A comparison is also made with the results of a nonrelativistic Thomas-Fermi (NR-TF) approximation.

THEORY

In the following discussion, the three numerical calculations will be described together with the methods used in calculating total energies. These descriptions will be followed by a discussion of the Thomas-Fermi approximation.

In the hitherto unreported BLW calculation, no exchange term appears in the (NR-H) potential function. In this calculation the total energy is approximated by use of the Slater I, F^k, and G^k integrals, which include exchange, as described in Vol. I of Slater's book.[6]

The LWC wave functions are solutions of the coupled Dirac relativistic equations, in which the Slater $\rho^{1/3}$ approximation[7,8] for the exchange term is used in conjunction with the Latter[9] self-interaction correction, in constructing the central field potential. The total energies were calculated from the expressions described below.

First, consider the single eigenvalue ϵ_i of the Hartree-Fock equation, which is given by

$$\epsilon_i=\langle T_i+V_i\rangle+\sum_j V_{ij}+\sum_j W_{ij}, \tag{1}$$

where T_i is the kinetic energy of the ith electron, V_i is the potential energy of the ith electron with respect to the nucleus, $\sum_j V_{ij}$ is the average electrostatic potential energy of the ith electron with respect to the other electrons, and $\sum_j W_{ij}$ is the average exchange potential energy of the ith electron with respect to the other electrons. The total energy E_T is then equal to

$$E_T=\sum_i \epsilon_i-\tfrac{1}{2}\sum_{ij} V_{ij}-\tfrac{1}{2}\sum_{ij} W_{ij}, \tag{2}$$

since pair interaction is counted twice. Consider the direct potential of the ith electron to be given by

$$\sum_j V_{ij}=\sum_j \int \psi_j^*(r')\frac{1}{|r-r'|}\psi_i(r)\psi_j(r')d^3r'$$

$$=\int \frac{\rho(r')}{|r-r'|}d^3r'\psi_i(r)\equiv V(r)\psi_i(r), \tag{3}$$

where, $\psi_i(r)$ is a two-component spin orbital representing the wave function for the ith electron, and

$$\rho(r')=\sum_j \psi_j^*(r')\psi_j(r').$$

Then,

$$\sum_{ij} V_{ij}=\sum_i \int \psi_i^*(r)V(r)\psi_i(r)d^3r$$

$$=\int \rho(r)V(r)d^3r. \tag{4}$$

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Now consider the exchange potential of the ith electron $\sum_j W_{ij}$ to be given by

$$\sum_j W_{ij} = -\sum \delta_{\sigma_i\sigma_j} \int \psi_j^*(r') \frac{1}{|r-r'|} \psi_j(r)\psi_i(r')d^3r'. \quad (5)$$

In Slater's method, summation over j and integration over r' can be replaced by the expression

$$\sum_j W_{ij} \simeq W(r)\psi_i(r),$$

where $W(r)$ is the free-electron exchange potential, namely

$$W(r) \equiv -(81/8\pi)^{1/3}[\rho(r)]^{1/3}. \quad (6)$$

Thus,

$$\sum_{ij} W_{ij} \simeq \sum_i \int \psi_i^*(r) W(r) \psi_i(r) d^3r$$

$$= \int \rho(r) W(r) d^3r, \quad (7)$$

and the total energy is then

$$E_T \simeq \sum_i \epsilon_i - \tfrac{1}{2} \int \rho(r)[V(r)+W(r)]d^3r, \quad (8)$$

which is the expression used in this method.

The HS wave functions are solutions of the so-called Hartree-Fock-Slater equations since the Slater $\rho^{1/3}$ approximation of exchange and the Latter self-interaction correction are employed in the (NR-HFS) potential. The HS eigenfunctions were recomputed by using the program Herman and Skillman published.[2] Total energies were also calculated using the HS eigenfunction by the same method as that used in the LWC eigenfunctions. The main difference between these two calculations is that the HS solutions are nonrelativistic.

Using the Thomas-Fermi approximation, Scott[10] showed that the total energy E_{TF} of a free atom of atomic number Z is related to the potential V produced at the nucleus by the surrounding electron cloud by the expression

$$E_{TF} = \int V(Z) dZ \quad (9)$$

and that V is related to the Thomas-Fermi[11] potential ϕ by

$$V(Z) = Zd\phi/dr|_{r=0}.$$

The gradient $d\phi/dr|_{r=0}$ has been shown by Scott to be $-1.7936Z^{4/3}$ which gives as an expression of total energy

$$E_{TF} = -0.7687Z^{7/3}$$

(in atomic units). Scott and later March and Plaskett[12] made corrections to account for boundary effects and exchange which lead to the expression for total energy

$$E_{TF} = -0.7687Z^{7/3} + \tfrac{1}{2}Z^2 - 0.266Z^{5/3} \quad (10)$$

for the nonrelativistic case. This expression was used in calculating the (NR-TF) total energies.

RESULTS AND DISCUSSIONS

Table I gives the total energies E_T for the normal ground state of the elements with atomic numbers in the range 2 to 36 for the self-consistent (NR-H), (NR-HFS), and (R-DS) calculations described above. Figure 1 gives the curves of energy versus atomic number for these three numerical calculations. Therein the (R-DS) curve is labeled LCW. In the same figure, points are also given for Clementi's and for Watson's analytical (NR-HF) solutions.

TABLE I. Comparison of the total energies of low atomic number, free atoms.

	Nonrelativistic		Relativistic
	BLW (NR-H) $-E_T$ (Ry.)	HS (NR-HFS) $-E_T$ (Ry.)	LWC (R-DS) $-E_T$ (Ry.)
Helium	5.723403	5.755868	5.599126
Lithium	14.89197	14.45243	14.38286
Beryllium	29.18997	28.51049	28.46454
Boron	49.08519	48.15778	48.11982
Carbon	75.36043	74.15735	74.13347
Nitrogen	108.6992	107.1735	107.1777
Oxygen	149.7843	147.8756	147.9225
Fluorine	199.2962	196.9160	197.0350
Neon	257.9155	254.9587	255.1814
Sodium	324.7861	321.1638	321.5484
Magnesium	400.5313	396.3616	396.9741
Aluminum	485.2652	480.5428	481.4286
Silicon	579.4141	574.1268	575.3637
Phosphorus	683.2948	677.4286	679.1096
Sulfur	797.2583	790.7725	792.9992
Chlorine	921.6204	914.4536	917.3633
Argon	1056.708	1048.808	1052.532
Potassium	1201.752	1193.142	1197.862
Calcium	1357.265	1348.033	1353.955
Scandium	1523.321	1513.684	1520.993
Titanium	1700.687	1690.624	1699.582
Vanadium	1889.630	1879.218	1890.033
Chromium	2090.317	2079.636	2092.599
Manganese	2303.446	2292.255	2307.735
Iron	2528.877	2517.282	2535.593
Cobalt	2767.050	2755.001	2776.529
Nickel	3018.249	3005.750	3030.850
Copper	3282.825	3269.843	3298.948
Zinc	3560.796	3547.192	3580.873
Gallium	3851.847	3837.523	3876.316
Germanium	4156.293	4141.200	4185.716
Arsenic	4474.261	4458.455	4509.257
Selenium	4805.937	4789.378	4847.161
Bromine	5151.519	5134.158	5199.642
Krypton	5511.164	5492.977	5566.928

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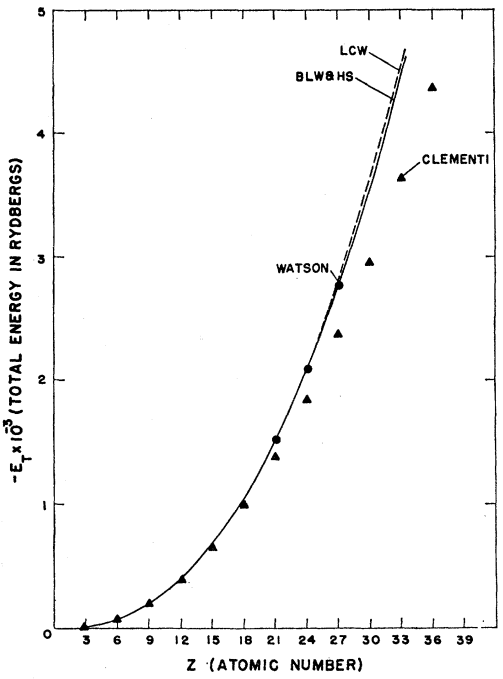

FIG. 1. Variation of the total energy as a function of atomic number in the range $Z \leq 36$ for the BLW, HS, and LWC numerical self-consistent field solutions. Also plotted are every third point for Clementi's and for Watson's analytical (NR-HF) solutions.

It can be seen in Fig. 1 that the results of all calculations are comparatively close, up to about aluminum. From that point, the three numerical calculation results agree fairly closely with the Watson analytical (NR-HF) solution. However, Clementi's (NR-HF) results begin to deviate at that point and become significantly lower at krypton. Although not shown in Fig. 1, the results of the (NR-TF) and the (NR-HFS) of HS agree within 2 Ry throughout this range of Z.

It is also evident from Table I that there is a slight difference between the BLW Hartree values and the HS Hartree-Fock-Slater values. The main difference between these two calculations apparently arises from the methods of calculating the total energy. The method used for E_T in the HS calculations gives total energies of smaller magnitude than does the method using the proper combination of Slater integrals. In order to make a more valid comparison, the Slater I integrals and total electron densities from the BLW wave functions were also used in the method for E_T outlined above to estimate the electrostatic and exchange corrections. That is, the total energy was calculated by considering

$$I_i = \langle T_i + V_i \rangle, \tag{11}$$

$$\therefore E'_T = \sum_i I_i + \tfrac{1}{2} \sum_{ij} V_{ij} + \tfrac{1}{2} \sum_{ij} W_{ij}. \tag{12}$$

The typical results of four elements are given in Table II. It can be seen that there is an appreciable difference

TABLE II. Comparison of total energies obtained two ways with BLW wave functions.

	(Slater I with angularly dependent F^k and G^k integrals)	(Slater I integrals and LWC E_T method)	% difference
Helium	5.723403	5.439943	4.95
Aluminum	485.2652	480.56083	0.97
Chromium	2090.317	2079.607	0.51
Krypton	5511.164	5492.945	0.33

between the results for elements of low atomic numbers, but less than 1% difference for elements with atomic numbers larger than that for aluminum.

One may expand

$$\frac{1}{|r-r'|} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} P_k(\cos\gamma), \tag{13}$$

where $r_<$ is $\min(r,r')$ and $r_>$ is $\max(r,r')$ and where γ is the angle between r and r'. In the method outlined above only the dominant term appropriate for a spherical average (namely, with $k=0$) is used and the angular dependence of orbitals is neglected. However, in making the perturbation corrections for electrostatic and exchange interactions to the BLW (NR-H) total energy, we have used the proper linear combination of F^k and G^k integrals (i.e., with $0 \leq k \leq l_1+l_2$, where l_1 and l_2 are the angular momenta of the two orbitals).

Table III gives the total energies for the normal ground state of the elements with atomic numbers 37 to 102 for the BLW and LWC calculations. Figure 2 is

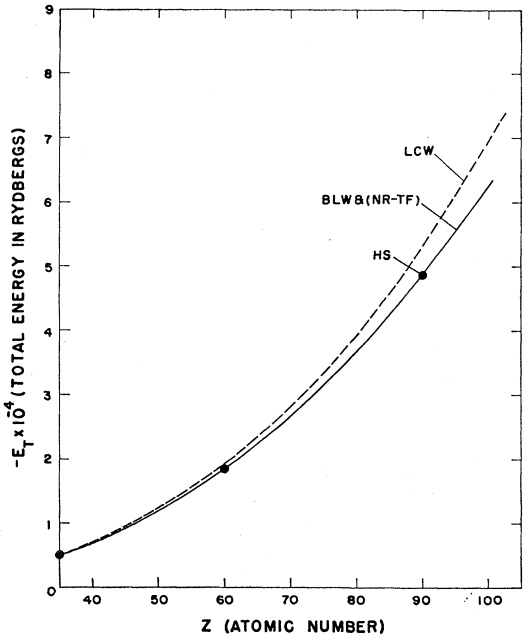

FIG. 2. Variation of the total energy as a function of atomic number in the range $35 \leq Z \leq 103$ for the LWC and BLW numerical solutions and for the (NR-TF) approximations. Also plotted are three results for the Herman-Skillman (NR-HFS) solutions.

TABLE III. Comparison of the best nonrelativistic and relativistic total energies.

Atomic No.	Symbol	BLW (NR-H) $-E_T$(Ry.)	LWC (R-DS) $-E_T$(Ry.)	Atomic No.	Symbol	BLW (NR-H) $-E_T$(Ry.)	LWC (R-DS) $-E_T$(Ry.)
37	Rb	5884.120	5948.433	70	Yb	26 790.93	28 118.75
38	Sr	6270.831	6344.676	71	Lu	27 711.99	29 128.41
39	Y	6671.286	6755.713	72	Hf	28 650.08	30 160.98
40	Zr	7086.023	7182.037	73	Ta	29 606.98	31 216.78
41	Nb	7515.214	7632.832	74	W	30 582.21	32 296.11
42	Mo	7959.148	8081.506	75	Re	31 575.74	33 399.23
43	Tc	8417.816	8555.174	76	Os	32 588.15	34 526.51
44	Ru	8891.750	9045.133	77	Ir	33 619.02	35 678.29
45	Rh	9380.742	9551.567	78	Pt	34 669.17	36 854.92
46	Pd	9885.273	10 074.80	79	Au	35 737.85	38 056.81
47	Ag	10 405.05	10 641.88	80	Hg	36 824.89	39 284.19
48	Cd	10 940.09	11 171.96	81	Tl	37 930.54	40 536.92
49	In	11 490.43	11 745.84	82	Pb	39 054.76	41 815.68
50	Sn	12 056.19	12 336.93	83	Bi	40 197.88	43 120.71
51	Sb	12 637.51	12 945.41	84	Po	41 359.73	44 452.49
52	Te	13 234.51	13 571.29	85	At	42 540.66	45 811.42
53	I	13 847.31	14 215.39	86	Rn	43 740.39	47 197.93
54	Xe	14 476.02	14 877.31	87	Fr	44 958.67	48 611.95
55	Cs	15 119.95	15 556.82	88	Ra	46 195.44	50 054.17
56	Ba	15 779.46	16 254.40	89	Ac	47 451.08	51 524.94
57	La	16 454.70	16 970.23	90	Th	48 725.72	53 024.97
58	Ce	17 145.71	17 704.96	91	Pa	50 019.80	54 554.87
59	Pr	17 853.86	18 459.21	92	U	51 333.53	56 115.77
60	Nd	18 578.84	19 233.16	93	Np	52 667.03	57 707.91
61	Pm	19 320.88	20 027.07	94	Pu	54 020.61	59 332.09
62	Sm	20 080.10	20 841.25	95	Am	55 394.05	60 988.83
63	Eu	20 856.67	21 675.93	96	Cm	56 787.27	62 678.77
64	Gd	21 650.66	22 531.26	97	Bk	58 200.96	64 402.80
65	Tb	22 462.43	23 408.05	98	Cf	59 635.45	66 161.62
66	Dy	23 291.93	24 306.10	99	Es	61 088.34	67 956.08
67	Ho	24 139.36	25 225.88	100	Fm	62 564.37	69 786.97
68	Er	25 004.94	26 167.70	101	Md	64 059.92	71 655.21
69	Tm	25 888.73	27 131.88				

a plot of E_T versus atomic number for these two calculations. Also shown in the figure is a plot of the (NR-TF) approximations and three points of the HS calculations. Again, these four calculation results are comparatively close throughout the range of atomic numbers, except that the results for the LWC relativistic calculations are higher at large values of Z. Of course, this increase in difference at higher atomic numbers is to be expected, since the relativistic effects are more significant in the heavier elements.

A better indication of how this difference due to relativistic effects varies with Z is found in comparison of the results of the Herman-Skillman (NR-HFS) with the Liberman-Waber-Cromer (R-DS) calculations. Table IV gives such a comparison of several elements with atomic numbers ranging from 58 to 62 and from 90 to 94. From this table it is evident that the difference increases uniformly with increasing atomic number, as is expected.

TABLE IV. Comparison of nonrelativistic and relativistic values of E_T based on free electron estimate of exchange.

	Herman-Skillman (NR-HFS)	Liberman-Waber-Cromer (R-DS)	% difference
Cerium	17 114.10	17 704.96	3.34
Praseodymium	17 822.23	18 459.21	3.45
Neodymium	18 547.22	19 233.16	3.57
Promethium	19 289.26	20 027.07	3.68
Samarium	20 048.59	20 841.25	3.80
Thorium	48 685.93	53 024.97	8.18
Protactinium	49 980.51	54 554.87	8.38
Uranium	51 294.42	56 115.77	8.59
Neptunium	52 628.10	57 707.91	8.80
Plutonium	53 982.08	59 332.09	9.02

CONCLUSIONS

In view of the differences among approximations made in the self-consistent field calculations, it is felt that the results of the total energy calculations presented here are in good agreement.

It was found that, if the same Slater I integrals and, total electron densities are used to calculate total energies both by the LWC method described above and by means of the Slater F^k and G^k integrals, there is an appreciable difference between the results for elements of low atomic number. However, this difference is less than 1% for elements having atomic numbers higher than that of aluminum.

It was also found that the Hartree calculations (with perturbation estimates of the exchange contribution) give total energies of larger magnitude than do the Hartree-Fock-Slater calculations. For example, the

Hartree total energy is larger by as much as 38.53 Ry for plutonium.

Total energies calculated from the relativistic solutions are of about the same magnitude as those obtained from the nonrelativistic solutions at low values of atomic number, but are significantly larger at high atomic numbers. This difference increases uniformly with increasing atomic number from 1.06% for germanium to 9.02% for plutonium.

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Magnetic Susceptibility of 2 $^3S_1$ State of Helium and Some Like Ions

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The magnetic susceptibility of the 2 $^3S_1$ state of helium and some like ions is computed using a thirty-five term wave function of the type originally proposed by Hylleraas and Undheim. It is found that it is possible to obtain highly accurate values for the magnetic susceptibility using this wave function if the parameters are accurately determined. Finally, an argument is given which suggests that the magnetic susceptibility obtained in the present work is accurate to at least five significant figures.

I. INTRODUCTION

IN atomic helium the only electronic states of practical importance are those for which at least one electron is in the ground state. Thus, as is well known,[1] the Pauli antisymmetry principle is satisfied for wave functions for which either the spatial function is symmetric and the spin function is antisymmetric or for wave functions having antisymmetric spatial functions and symmetric spin functions. These two possibilities lead to two term schemes, the former giving the singlet system whose lowest member is 1 $^1S_0$ while the latter leads to the triplet system whose lowest member is 2 $^3S_1$.

Inasmuch as the 2 $^3S_1$ triplet state lies above the ground state by 19.8 eV and transitions to the ground state 1 $^1S_0$ are rather rigorously forbidden, both by the orthogonality of the spin functions and by the symmetry differences of the spatial functions, this metastable state has of late been the subject of a number of investigations. Experimentally this state is an attractive metastable system to study as it is possible to obtain an appreciable concentration of these metastable atoms under experimental conditions. From the point of view of the theorist it is attractive as an approximate wave function and triplet state energy are obtained in which the energy is a rigorous upper bound to the true triplet energy simply by requiring that the spatial part of ones variational wavefunction be antisymmetric.

To mention just a few of the recent papers on 2 $^3S_1$ helium, Pekeris,[2] Hart and Herzberg,[3] Davis,[4,5] and Traub and Foley[6] have all made accurate variational calculations of the energy. Hughes[7–9] and his coworkers have made rather definitive experimental and theoretical studies of the magnetic moment in this state. Finally, Benton, Ferguson, Matsen, and Robertson[10] have recently made a number of measurements of the cross sections for de-excitation of the metastable atom by collisions with other atoms.

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