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Atomic Energy Levels for the Thomas-Fermi and Thomas-Fermi-Dirac Potential*

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The eigenvalues of the Schrödinger equation have been obtained for the Thomas-Fermi and Thomas-Fermi-Dirac atomic potentials. Electron self-interactions were taken into account by modifying the potentials to give asymptotically the field of a unit charge. All levels were treated from 1*s* to 7*d* for a range of *Z*-values sufficient to permit easy interpolation. It was found that the energies, for either the Thomas-Fermi or Thomas-Fermi-Dirac potentials, agree in general as well with experimental ionization energies as the Hartree or Hartree-Fock approximations. Applications of the statistical potential to other atomic problems are indicated.

I. INTRODUCTION

QUANTITATIVE estimates of atomic behavior rely heavily upon the self-consistent field method of Hartree[1] and Hartree-Fock[2] for the determination of atomic states. These methods provide the best solution for the atomic ground state in terms of a separable wave function in the sense that this solution is derived from a variational principle which minimizes the total energy. This extremum property cannot be claimed, in general, for excited states since they must be orthogonal to all lower states, and this orthogonality may require a superposition of product type wave functions.

The numerical complexity of the Hartree and Hartree-Fock methods makes it difficult to obtain an overall picture of atomic behavior. At present only isolated solutions of the self-consistent field equations are available, and these mainly for ground state configurations. The difficulty in the methods lies primarily in the lengthy numerical iterations which lead to the self-consistent solutions. Straightforward iterations in the Hartree procedure are not necessarily convergent so that in practice additional numerical complications arise.

It is suggested, however, that these numerical difficulties in the Hartree, or Hartree-Fock, procedure will not be circumvented without loss of accuracy, at least for the ground state configuration. For the excited states it may be possible to find a mathematically simpler method without loss of accuracy since in this case the Hartree procedure is not necessarily optimal. For the ground state, though, the method does give, in principle, the best possible value for the total energy of the atom, subject to the limitation of separable wave functions. Even if the total energy of the atom has been determined accurately, it does not follow that all single electron term values have been accurately determined. In fact, the lowest one-electron term value will be weighted most heavily in the total energy determination for the atom, and presumably is very accurate. Higher single electron term values, which contribute less importantly to the total atom energy, may be only roughly determined. In view of these features of the Hartree, or Hartree-Fock, approximation, consideration has been given to simpler approximations which could be applied to atomic systems in their ground states. An approximation with this general applicability is furnished by the use of the Thomas-Fermi,[3] or Thomas-Fermi-Dirac,[4] statistical potential as a central field for the atomic system. Some term values for circular orbits and for the 5*f* level have been determined by previous investigators[5,6] with this potential, but a general exploration of the results to be obtained has not previously been carried out. The results of such an exploration will be presented here for the isolated, zero-temperature atom for all atomic numbers and for the one-electron term values from 1*s* to 7*d*.

II. THEORETICAL CONSIDERATIONS

The description of the many-electron atom which uses an equivalent central potential, such as a statistical potential, is familiar in spectroscopy as the central-field approximation.[7] In this approximation, an equivalent central potential is used to generate a set of energy levels and wave functions under the assumption that the electrons are independent. The one-electron wave functions and energy levels so obtained may be taken as the zero order basis to which corrections can be applied by perturbation theory. The one-electron eigenfunctions and eigenvalues are given by solution of the Schrödinger equation,

$$[-(\hbar^2/2m)\Delta - eV(r)]\phi_i = \epsilon_i\phi_i, \qquad (1)$$

where $V(r)$ is the effective central potential for the atom. In the present discussion, this potential is either the Thomas-Fermi, or the Thomas-Fermi-Dirac, statistical potential. In this zero order, the total energy

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[1] D. R. Hartree, Proc. Cambridge Phil. Soc. **24**, 89 (1928).

[2] V. Fock, Z. Physik **61**, 126 (1930).

[3] E. Fermi, Atti. accad. nazl. Lincei **6**, 602 (1927); **7**, 342, 726 (1928); L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927).

[4] P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930).

[5] F. Rasetti, Atti accad. nazl. Lincei **7**, 915 (1928); Z. Physik **49**, 546 (1928); R. Gáspár, J. Chem. Phys. **20**, 1863 (1952).

[6] Maria G. Mayer, Phys. Rev. **60**, 184 (1941).

[7] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1951).

of the atom is given by

$$E=\sum_{\{i\}}\epsilon_i, \tag{2}$$

and the wave function for the atom, without antisymmetrization, is

$$\psi=\prod_{\{i\}}\phi_i, \tag{3}$$

where $\{i\}$ denotes the set of occupied one-electron levels. This form for the total energy, or for the total wave function, is assumed to apply to the ground state as well as to excited configurations. The analytic simplicity resulting from this assumption is evident and is a consequence of using a fixed potential for all configurations. With the aim of obtaining similar simplicity in the Hartree methods, Roothaan[8] has proposed that the Hartree ground state potential be used as the fixed potential with which excited configurations are determined. This simplification of the Hartree procedure carries with it, however, the numerical difficulties associated with the determination of the Hartree ground state.

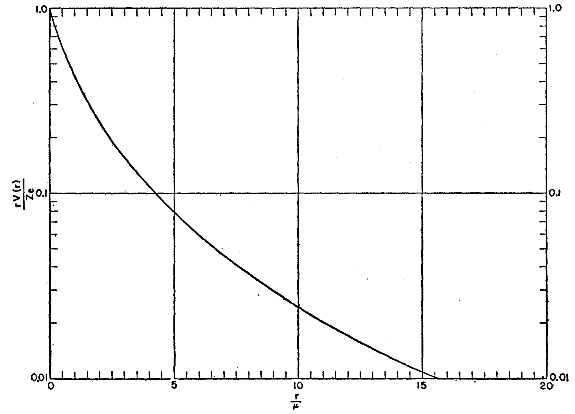

FIG. 1. The potential distribution for the Thomas-Fermi atom.

The important error in this application of a fixed central field arises just from the use of the same potential for all configurations of the atom. This error clearly grows with increasing excitation of the atom above the ground state. It will be apparent from the results to be presented here that the statistical potentials give acceptable values for ground state energies and presumably will therefore give semiquantitative predictions for states of low excitation. If highly excited atomic states are determined in this way, the perturbation corrections to the energies and wave functions will certainly become important. These perturbation corrections are determined by the perturbation energy operator,

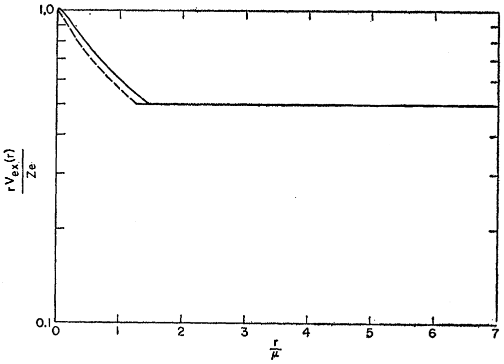

FIG. 2. The potential distribution for the Thomas-Fermi-Dirac atom is shown with the solid line; the dashed line shows the approximation of the universal function of Eq. (9) for $Z=2$.

$$H_{\text{pert}}=\sum_i\left\{eV(r_i)-\frac{Ze^2}{r_i}+\tfrac{1}{2}\sum_{i\neq j}\frac{e^2}{r_{ij}}+\sum_i\xi(r_i)\mathbf{L}_i\cdot\mathbf{S}_i\right\}, \tag{4}$$

where customary notation[7] has been used. In the present paper, however, the evaluation of term values is limited to the zeroth order even for excited states.

III. DETERMINATION OF THE ATOMIC POTENTIAL

The effective central field potential used in the present calculations is estimated from the statistical model of Thomas-Fermi and from the statistical model including exchange as developed by Dirac. More specifically, these statistical potentials are taken for the isolated atom at absolute zero temperature so that the ground state potential of the atom is the potential under discussion. The potential distribution for the Thomas-Fermi atom, without exchange, has been calculated by Miranda,[9] and has been recalculated with improved accuracy by the author.[10] The analytic fit to this potential function was used for the present calcu-

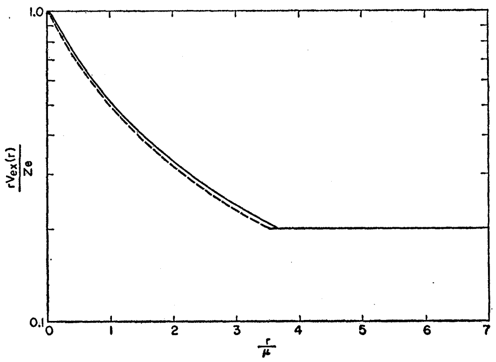

FIG. 3. The potential distribution for the Thomas-Fermi-Dirac atom is shown with the solid line; the dashed line shows the approximation of the universal function of Eq. (9) for $Z=5$.

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

[9] C. Miranda, Mem. Acc. Italia **5**, 285 (1934).

[10] Unpublished calculations.

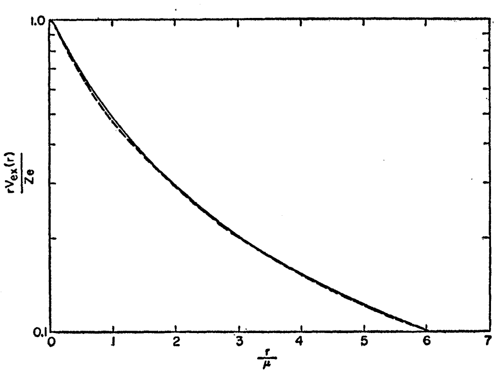

FIG. 4. The potential distribution for the Thomas-Fermi-Dirac atom is shown with the solid line; the dashed line shows the approximation of the universal function of Eq. (9) for $Z=10$.

lations:

$$\phi(r/\mu)=\frac{rV(r)}{Ze}=\Big[1+0.02747(r/\mu)^{\frac{1}{2}}+1.243(r/\mu)-0.1486(r/\mu)^{\frac{3}{2}}+0.2302(r/\mu)^2+0.007298(r/\mu)^{5/2}+0.006944(r/\mu)^3\Big]^{-1}, \quad (5)$$

where $\mu=0.8853a_0/Z^{\frac{1}{3}}$ and a_0 is the Bohr radius. The maximum error in this fit to the numerical values is less than 0.3 percent. The potential of Eq. (5) includes the electrostatic self-interaction of the electron whose term value is to be determined, and consequently it leads to significant errors in the higher term values. A number of modifications in the Thomas-Fermi potential have been suggested[11] to remove this source of error in applications to the atomic term-value problem. The Thomas-Fermi ion potential and the Fermi-Amaldi correction have been proposed as more correct fields. These latter have the practical disadvantage of requiring a new solution of the Thomas-Fermi equation for each value of Z. A procedure which does not have this disadvantage replaces the $V(r)$ of Eq. (5) by

$$V(r)=[(Z-1)e\phi(r/\mu)+e]/r, \quad (6)$$

where $\phi(r/\mu)$ is the universal Thomas-Fermi[12] function for the neutral atom of atomic number Z. The predictions of the potential of Eq. (6) for the behavior of the $4f$ and $5f$ electrons have been obtained by Mayer.[6] More extended calculations by the present author with this potential indicated that it over-corrected appreciably for the self-interaction; it consequently gives too large binding energies.

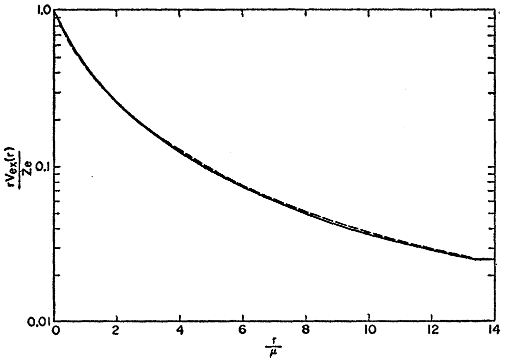

FIG. 5. The potential distribution for the Thomas-Fermi-Dirac atom is shown with the solid line; the dashed line shows the approximation of the universal function of Eq. (9) for $Z=40$.

The potential which was used in the present calculations was

$$V(r)=Ze\frac{\phi(r/\mu)}{r}, \quad \text{if} \quad V(r)>\frac{e}{r}, \quad (7)$$
$$V(r)=0, \quad \text{otherwise},$$

and as shown in Fig. 1. This form of potential, which provides the correct asymptotic behavior, was adopted for reason of simplicity. It does not make any modification in the field for self-interaction in the interior of the atom, but over most of this region this neglect should be relatively unimportant.

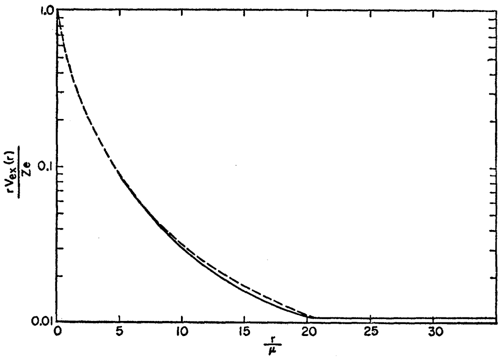

FIG. 6. The potential distribution for the Thomas-Fermi-Dirac atom is shown with the solid line; the dashed line shows the approximation of the universal function of Eq. (9) for $Z=92$.

The Thomas-Fermi potential of Eq. (7) estimates only the electrostatic interaction of the electrons for the atomic ground state. The Dirac extension of the Thomas-Fermi model provides an approximate procedure for including exchange effects. If $\phi_{\text{ex}}(r/\mu)$ is the solution for the Thomas-Fermi-Dirac equation,[13] then the effective central field[14] for the one-electron

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[11] P. Gombas, *Die Statistische Theory des Atoms* (Springer-Verlag, Berlin, 1949).

[12] P. Gombas (reference 11). The function $\phi(r/\mu)$ used here is the same as Gombas' $\phi(x)$.

[13] P. Gomas (reference 11). The function $\phi_{\text{ex}}(r/\mu)$ used here is the same as Gombas' $\psi(x)$.

[14] The physical implications of the discontinuity in the $V(r)$ of Eq. (8) have been discussed by N. H. March, Phil. Mag. **45**, 325 (1954).

Schrödinger equation is

$$V_{\mathrm{ex}}(r)=Ze\frac{\phi_{\mathrm{ex}}(r/\mu)-\phi_{\mathrm{ex}}(r/\mu)(r/r_0)}{r}$$

$$+\frac{Z^{\frac{1}{2}}e}{r_0}\frac{3\sqrt{2}}{2\pi}\left(\frac{r_0}{a_0}\right)^{\frac{1}{2}}\left[\left(\frac{\phi_{\mathrm{ex}}(r/\mu)}{r/r_0}\right)^{\frac{1}{2}}+\delta\right], \quad (8)$$

$$\text{for} \quad r<r_0,$$

$$V_{\mathrm{ex}}(r)=0, \quad \text{for} \quad r>r_0,$$

where $\delta=(3/32\pi^2)^{\frac{1}{3}}(1/Z^{\frac{2}{3}})(r_0/\mu)^{\frac{1}{2}}$. It should be noted that $\phi_{\mathrm{ex}}(r/\mu)$ is the solution of the Thomas-Fermi-Dirac equation for prescribed Z which corresponds to zero pressure at the boundary of the atom; r_0 is the finite radius of the atom required as a consequence of the zero-pressure boundary condition. The first term of Eq. (8) is the electrostatic potential and the second term is the effective exchange potential. As is familiar, the electronic self-interactions are correctly eliminated within the framework of the Thomas-Fermi-Dirac model. In the present application, where the Thomas-Fermi-Dirac potential of Eq. (8) is used as the atomic central field in the Schrödinger equation, it does not properly account for the electron self-interaction since it does not possess the correct asymptotic behavior. The potential was therefore modified by the same procedure as was used to get the potential of Eq. (7). The practical difficulty still remains that separate solutions of the Thomas-Fermi-Dirac equation for $\phi_{\mathrm{ex}}(r/\mu)$ are required for each value of Z. This difficulty

TABLE I. Term values in Rydbergs computed with the Thomas-Fermi potential of Eq. (7).

Z	$1s$	$2s$	$2p$	$3s$	$3p$	$3d$	$4s$	$4p$	$4d$	$4f$	$5s$	$5p$
2	1.250×10^{0}	2.775×10^{-1}		1.190×10^{-1}			6.578×10^{-2}					
3	2.665	3.606	2.516×10^{-1}	1.402			7.419				4.582×10^{-2}	
4	5.701	4.329	2.553	1.568	1.129×10^{-1}		8.041	6.331×10^{-2}				
5							8.612					
6	1.628×10^{1}	6.321	2.781	1.950	1.207	1.111×10^{-1}	9.374	6.668			5.494	4.216×10^{-2}
7			3.146		1.321			7.137				
8	3.307	1.312×10^{0}	4.220		1.560		1.139×10^{-1}				6.358	4.871
9		1.976	7.078	2.940	1.840		1.226	8.937				
10	5.637	2.871	1.231×10^{0}	3.231	2.027							5.554
11	7.053	3.992	1.986	3.527	2.152	1.113	1.378	9.950			7.314	
12				3.871	2.254							
13	1.040×10^{2}	6.957	4.195	4.323	2.357	1.114	1.563	1.063×10^{-1}	6.265×10^{-2}		8.021	6.039
14				4.970	2.480			1.104				
15								1.158				6.450
16	1.671	1.334×10^{1}	9.379	7.344	2.925		2.028					
17		1.603		9.317				1.350				7.211
18					4.251							
19	2.462	2.227	1.703×10^{1}	1.516×10^{0}	5.654	1.118	2.548	1.637	6.294		1.112×10^{-1}	8.213
22					1.386×10^{0}		3.012	1.939				
23				3.482		1.128			6.354			9.463
24												
25						1.149			6.518			
26	4.934	5.392	4.556	5.713	3.445	1.240	3.902	2.216	7.522		1.461	1.013×10^{-1}
27						2.773			1.060×10^{-1}			
28						5.951						
29	6.268	7.245	6.269	8.667	5.777	1.005×10^{0}	5.378	2.522	1.103	6.250×10^{-2}	1.730	1.113
30						1.499						
31								2.930				
32								3.273			2.056	
33								3.768				1.387
35						5.244	1.363×10^{0}	5.388	1.122		2.359	1.561
37	1.063×10^{3}	1.373×10^{2}	1.238×10^{2}	2.054×10^{1}								
38					1.752×10^{1}	8.572	2.114		1.131		2.639	
40								1.394×10^{0}	1.142		2.836	1.902
41												
42									1.168		3.067	
44									1.320		3.359	2.054
45												
46									3.021		3.760	
47	1.777	2.517	2.332	4.475	3.751	2.404×10^{1}	5.934	3.767	4.652	6.250	4.021	2.218
50											5.163	2.470
52									1.797×10^{0}			2.754
53												2.957
54											7.961	
57	2.679	4.046	3.813	8.070	7.072	5.190	1.350×10^{1}	9.996	3.981	6.251	1.124×10^{0}	4.524
60											1.554	
61										6.251		7.838
63										6.251		
65	3.537	5.558	5.285	1.186×10^{2}	1.064×10^{2}	8.308	2.252	1.785×10^{1}	9.461	6.252	2.529	1.314×10^{0}
66										6.254		
67										3.391×10^{-1}		
68										7.735		1.849
70										1.789×10^{0}		2.274
72										2.995		
74	4.648	7.571	7.253	1.717	1.568	1.283×10^{2}	3.632	3.020	1.894×10^{1}	4.391	5.188	3.299
76											5.957	
77												4.231
78										7.758	6.795	
82	5.765	9.642	9.284	2.285	2.111	1.779	5.212	4.462	3.065	1.191×10^{1}	8.692	6.125
84												
87										1.826	1.150×10^{1}	8.478
88												
92	7.334	1.261×10^{3}	1.220×10^{3}	3.127	2.922	2.530	7.690	6.760	5.007	2.594	1.482	1.133×10^{1}

TABLE I.—*Continued.*

Z	$5d$	$5f$	$5g$	$6s$	$6p$	$6d$	$6f$	$6g$	$6h$	$7s$	$7p$	$7d$
2												
3				3.108×10^{-2}						2.246×10^{-2}		
4												
5												
6				3.605	2.903×10^{-2}					2.546	2.120×10^{-2}	
7												
8				4.053	3.269						2.344	
9										2.911		
10												
11				4.531	3.731					3.080	2.620	
12												
13					3.890	2.783×10^{-2}				3.267	2.713	2.044×10^{-2}
14												
15												
16				5.584	4.265							
17												
18												
19	4.026×10^{-2}				4.948	2.794				3.994	3.307	2.051
22												
23	4.063			6.968	5.516	2.817					3.612	2.067
24	4.091					2.835						2.079
25	4.169					2.887						2.114
26	4.887					3.352				4.692		2.418
27	6.009					3.872						2.702
28	6.152					3.946						2.745
29	6.203			8.611	6.255	3.974				5.140	4.001	2.762
30												
31	6.252											
32	6.268											
33												
35				1.058×10^{-1}	7.931	4.037				6.004	4.811	
37												2.814
38	6.371					4.072						
40	6.444					4.116						2.850
41	6.510					4.158						2.877
42	6.628			1.260	9.298	4.235				6.848	5.440	2.926
44	7.886					4.986						3.373
45	9.667					5.646						3.688
46	1.041×10^{-1}					5.915						3.819
47	1.069	4.000×10^{-2}		1.487	1.017×10^{-1}	6.033				7.721	5.832	3.881
50	1.097					6.175						3.957
52				1.830	1.175					8.898	6.498	
53												
54												
57	1.121	4.000		2.176	1.456	6.307	2.778×10^{-2}			9.987	7.537	4.033
60		4.001				6.366						
61												
63	1.145	4.001				6.460	2.778			1.112×10^{-1}		4.124
65	1.161	4.001		2.691	1.809	6.577	2.779			1.152	8.758	4.196
66		4.004					2.782					
67	1.197	6.249				6.848	4.000					4.363
68	1.238	6.250				7.165	4.000			1.220	9.099	4.555
70	1.529	6.251				8.808						5.307
72	2.724					1.014×10^{-1}	4.001					5.792
74	4.755	6.251	4.000×10^{-2}	3.704	2.128	1.058	4.001	2.778×10^{-2}	2.778×10^{-2}	1.410	9.854	5.978
76												
77												
78	1.077×10^{0}	6.251			2.359	1.089				1.591	1.059×10^{-1}	6.132
82	1.931	6.251	4.000	6.365	2.788	1.104	4.001	2.778	2.778	1.797	1.175	6.212
84	2.455											
87					4.020						1.380	6.293
88	3.713											
92	5.265	6.252	4.000	1.460×10^{0}	6.609	1.135	4.002	2.778	2.778	2.268	1.573	6.393

may be obviated by the observation that the $V_{\mathrm{ex}}(r)$ of Eq. (8) may be approximated by a universal potential of the following form:

$$V_{\mathrm{ex}}(r)=Ze\frac{\phi(r/\mu)}{r}+\frac{3\sqrt{2}}{4\pi}\frac{Z^{\frac{1}{2}}e}{a_0^{\frac{1}{2}}}\frac{[\phi(r/\mu)]^{\frac{1}{2}}}{r^{\frac{1}{2}}}, \qquad \text{for} \quad V_{\mathrm{ex}}(r)>e/r. \tag{9}$$

$$V_{\mathrm{ex}}(r)=e/r, \quad \text{otherwise,}$$

where $\phi(r/\mu)$ is defined by Eq. (5), and where the proper cut-off behavior has been included. This universal exchange potential deviated from the Thomas-Fermi-Dirac potentials by less than 5 percent for $5<Z<92$; for values of $Z<5$ the error increases. A comparison of (9) with the Thomas-Fermi-Dirac potentials is shown in Figs. 2–6 for $Z=2$, 5, 10, 40, and 92.

IV. NUMERICAL PROCEDURE

The calculations for the term values with the potentials of Eqs. (7) and (9) were carried out by numerical integration of the Schrödinger equation on an IBM 701 Defense Calculator. If the wave function ϕ_i is written as

$$\phi_i=[\psi_i(r)/r]Y_{lm}(\theta,\phi), \tag{10}$$

then ψ_i satisfies the differential equation

$$\psi_i''-\left[\frac{2m\epsilon_i}{\hbar^2}-\frac{2me}{\hbar^2}V(r)+\frac{l(l+1)}{r^2}\right]\psi_i=0, \tag{11}$$

TABLE II. Term values in Rydbergs computed with the Thomas-Fermi-Dirac potential of Eq. (9).

Z	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p
2	1.613×10^{0}	3.048×10^{-1}		1.284×10^{-1}			6.881×10^{-2}					
3	3.818	3.886	2.569×10^{-1}	1.472			7.677				4.709×10^{-2}	4.055×10^{-2}
4	7.471	4.770	2.729	1.669	1.188×10^{-1}		8.398	6.585×10^{-2}				
5							9.366					
6	1.917×10^{1}	9.540	4.208	2.304	1.530	1.113×10^{-1}	1.044×10^{-1}	7.892			5.964	4.807
7			6.709		1.772			8.698				
8	3.711	2.166×10^{0}	1.100×10^{0}		1.953		1.226				6.699	
9		3.082	1.715	3.293	2.097		1.318	9.772				
10				3.743	2.241							5.872
11	7.633	5.540	3.546	4.387	2.420	1.120	1.563	1.083×10^{-1}			7.982	
12				5.336	2.680							
13	1.110×10^{2}	8.956	6.268	6.692	3.099	1.124	1.895	1.264	6.330×10^{-2}		9.100	6.861
14				8.518	3.789			1.389				
15								1.517	6.376			7.775
16	1.759	1.604×10^{1}	1.224×10^{1}	1.369×10^{0}	6.403		2.385					
17		1.898		1.707		1.144		1.732	6.460		1.110×10^{-1}	8.510
18					1.096×10^{0}				6.539			
19	2.567	2.570	2.070	2.554	1.403	1.176	2.922	1.907	6.694		1.216	9.117
20						1.229			7.131			
21						1.475			8.745			
22					2.668	2.500	3.843	2.205	1.024×10^{-1}		1.436	
23				5.018		4.351			1.070			1.056×10^{-1}
24									1.091			
25						1.004×10^{0}			1.104			
26	5.083	5.912	5.117	7.632	5.282		6.682	3.121	1.113		1.818	1.244
27						1.839						
28						2.363						
29	6.434	7.842	6.915	1.098×10^{1}	8.042	2.961	1.057×10^{0}	4.958	1.137	6.251×10^{-2}	2.103	1.469
30						3.639						
31								7.032	1.158			
32								8.348			2.469	
33								9.860	1.194			
34									1.229			
35						8.265	2.392	1.350×10^{0}	1.293		2.759	1.826
36									1.432			
37	1.085×10^{3}	1.454×10^{2}	1.325×10^{2}	2.393					1.745			
38					2.114×10^{1}	1.212×10^{1}	3.383		2.319		3.309	2.019
39												
40								2.662	4.250		3.862	2.185
41												
42									7.148		4.655	2.427
44											5.672	2.793
46											7.016	
47	1.805	2.625	2.450	4.964	4.257	2.918	7.949	5.656	1.883×10^{0}	6.253	7.808	3.720
50											1.068×10^{0}	5.270
52									3.776			6.711
53												7.558
54											1.588	
55												
56												
57	2.701	4.182	3.960	8.715	7.744	5.886	1.634×10^{1}	1.284×10^{1}	6.509	6.256	2.085	1.186×10^{0}
58										6.257		
59										6.275		
60										2.667×10^{-1}		
61											2.913	1.777
62												
63										1.297×10^{0}		
65	3.576	5.716	5.456	1.264×10^{2}	1.145×10^{2}	9.153	2.616	2.149	1.288×10^{1}	2.195	3.944	2.552
67												3.017
68										3.859		
70										5.184	5.558	3.816
72												
74	4.692	7.554	7.451	1.809	1.664	1.384×10^{2}	4.086	3.480	2.340	8.371	7.133	5.093
77												6.219
78										1.230×10^{1}	8.994	
80												
82	5.814	9.848	9.507	2.390	2.222	1.896	5.750	5.010	3.605	1.701	1.115×10^{1}	8.445
84												
85												
87												1.114×10^{1}
88										2.560		
89												
90												
91												
92	7.390	1.285×10^{3}	1.246×10^{3}	3.249	3.050	2.666	8.336	7.420	5.668	3.240	1.785	1.435

where $V(r)$ is either the potential of Eq. (7) or of Eq. (9). The scheme adopted for the numerical integration of Eq. (11) is similar to one recently suggested by Blanch.[15] Equation (11) was converted into the following integral equation:

$$\psi_i(r)=\psi_i'(0)r+\int_0^{r}(r-r')\left[\frac{2m\epsilon_i}{\hbar^2}-\frac{2me}{\hbar^2}V(r')+\frac{l(l+1)}{r'^2}\right]\psi_i(r')dr', \quad (12)$$

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[15] G. Blanch, Math. Tables and Other Aids to Computation **6**, 219 (1952).

TABLE II.—*Continued.*

Z	$5d$	$5f$	$5g$	$6s$	$6p$	$6d$	$6f$	$6g$	$6h$	$7s$	$7p$	$7d$
2												
3				3.179×10^{-2}	2.810×10^{-2}					2.290×10^{-2}	2.061×10^{-2}	
4												
5												
6				3.851	3.233					2.690	2.322	
7												
8				4.237	3.574							
9											2.595	
10										3.136		
11				4.872	3.935						2.740	
12												
13				5.387		2.807×10^{-2}				3.546	2.951	2.060×10^{-2}
14												
15	4.074×10^{-2}				4.739							
16										3.892	3.292	
17	4.125			6.253		2.856						2.092
18	4.173					2.887						2.113
19	4.273	4.000×10^{-2}		6.698	5.359	2.951				4.224	3.529	2.155
20	4.554					3.128						2.271
21	5.330					3.540						2.514
22	5.852					3.789						2.653
23	6.046			7.892	6.001	3.888				4.802	3.868	2.711
24	6.145					3.942						2.743
25	6.210				6.479	3.978						2.765
26	6.262	4.001				4.007				5.263	4.247	
27												2.798
28												2.815
29	6.404	4.001		9.810	7.578	4.090				5.670	4.640	2.833
30												
31	6.533					4.166						2.880
32	6.631				8.245	4.224				6.065		2.916
33	6.773					4.308					5.046	2.968
34	7.007					4.446						3.051
35	7.428			1.179×10^{-1}	8.835	4.677						3.185
36												
37	9.091					5.383				6.880		3.548
38	9.776				9.492	5.641					5.528	3.676
39	1.020×10^{-1}					5.808						3.761
40	1.046					5.922						3.820
41	1.064					6.005						3.865
42	1.077			1.563	1.075×10^{-1}	6.071				7.960	6.074	3.900
44					1.163							
46												
47	1.121	4.002		1.878	1.314	6.309				9.021	6.807	4.034
50	1.148					6.466						4.124
52	1.173			2.189	1.543	6.617				1.002×10^{-1}	7.815	4.211
53						6.722						4.271
54	1.212					6.861						4.350
55	1.244					7.050						4.454
56	1.290											
57	1.361	4.005		2.578	1.737	7.700	2.781×10^{-2}			1.120	8.508	4.782
58	1.480	4.006					2.783					
59	1.672	4.039				8.731	2.831					5.213
60		6.248					3.999					
61	2.366			3.055	1.910	9.614				1.246	9.114	5.553
62												5.672
63	3.502					1.013×10^{-1}	4.003					5.766
65	5.069	6.254		3.831	2.154	1.044	4.003			1.406	9.910	5.907
67												
68				4.709		1.074				1.539	1.072×10^{-1}	6.056
70	1.092×10^{0}	6.255			2.722	1.090					1.136	6.136
72				6.381			4.004					
74	1.778	6.256	4.000×10^{-2}	7.456	3.605	1.118	4.005	2.778×10^{-2}	2.778×10^{-2}	1.801	1.278	6.291
77												
78	2.686			1.012×10^{0}	5.052	1.152				1.972	1.414	6.484
80	3.229	6.257				1.176						6.620
82	3.837	6.258	4.000	1.355	7.098	1.209	4.007	2.778	2.778	2.155	1.533	6.812
84	4.511											
85		6.262				1.299						7.304
87		6.277		1.901	1.084×10^{0}	1.422	4.028				1.673	7.860
88	6.071	6.385				1.523	6.108			2.503		
89		2.071×10^{-1}										8.565
90		3.608					6.247					
91		5.340				2.082	6.250					9.214
92	7.930	7.263	4.000	2.597	1.579	2.372	6.252	2.778	2.778	2.839	1.828	9.474

where the boundary condition $\psi_i(0)=0$ has been used. For the numerical work, the integral equation was replaced by a difference equation. To insure stability of the difference equation, the integral which is the coefficient of r was evaluated by Cote's rule and the remaining integral was evaluated by Simpson's rule. Division points for the numerical integration were based on a scale of $r^{\frac{1}{2}}$, rather than on r, since the former scale makes the variations in the functions ψ_i more uniform. Improvements on initial guesses of the eigenvalues were obtained by a convergence procedure coded into the machine. This procedure automatically selected new guesses for the eigenvalues based on the requirement that the eigenfunction had the prescribed number

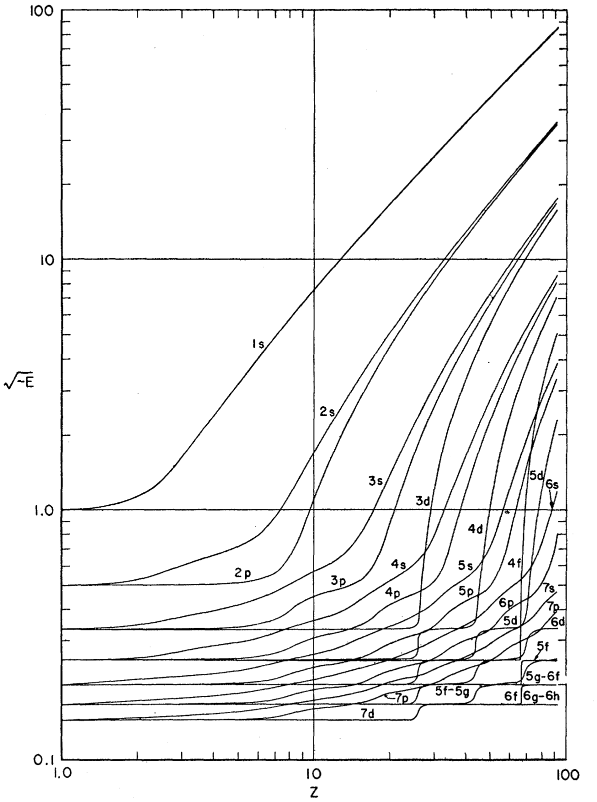

FIG. 7. The square root of the term values of Table I for the Thomas-Fermi atom is shown as a function of Z.

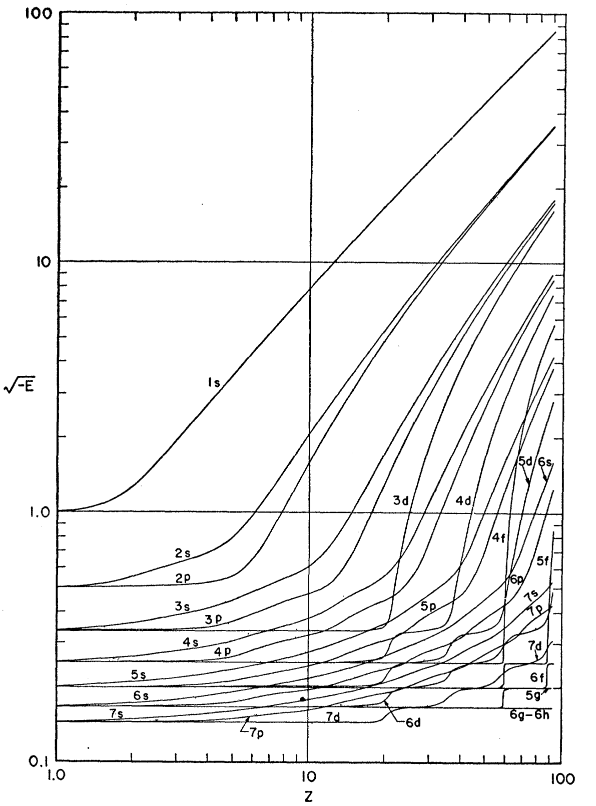

FIG. 8. The square root of the term values of Table II for the Thomas-Fermi-Dirac atom is shown as a function of Z.

of zeros and had a zero at a point distant from the origin where it was estimated to have a value less than 10^{-7} of its maximum value. The solution ψ_i will contain a small amplitude contribution from the irregular solution as a result of inevitable truncation and rounding errors in the numerical scheme. This error in the eigenfunction precludes the possibility of the solution being zero at the prescribed point. The accuracy of the eigenvalue determination is not affected by this difficulty. When the eigenvalue is known, this error in the eigenfunction may be avoided by integrating both inward and outward, and then joining the solutions at a point where the irregular solution is known to be negligible. This latter procedure is now in use in computations of eigenfunctions.

V. RESULTS AND CONCLUSIONS

The results of the present calculations for the one-electron term values $1s$ to $7d$ with the Thomas-Fermi potential of Eq. (7) are summarized in Table I. Similarly, the results for the same one-electron term values with the Thomas-Fermi-Dirac potential of Eq. (9) are shown in Table II. The values computed for Tables I and II include the minimum number of term values necessary to give a survey of the periodic table and also to permit easy graphical interpolation for those term values not tabulated. The numerical values of Tables I and II are shown graphically in Figs. 7 and 8, respectively. A more detailed presentation of the results is given in Figs. 9–12[16] which also include those Hartree, or Hartree-Fock, values which are available in the literature.[17] These figures also give a comparison of the computed values with experimental ionization energies taken from Landolt-Bornstein.[18]

The following conclusions are drawn from the computations with the statistical potentials:

1. There is a discrepancy at large binding energies between experimental term values and computed values whether computed with the statistical potential or with the Hartree procedure. This discrepancy is attributed to relativistic effects. An approximate correction for these relativistic effects was made by using the known

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[16] The levels $5g$, $6g$, and $6h$ are not included in these figures since these levels have hydrogenic term values.

[17] A survey of the existing results is given by D. R. Hartree, Repts. Progr. Phys. **11**, 8 (1946–47) and by Landolt-Bornstein (reference 18).

[18] Landolt-Bornstein, *Atom—und Molekularphysik* (Springer-Verlag, Berlin, 1950), Part I.

Note added in proof.—Recently J. C. Slater [Phys. Rev. **98**, 1039 (1955)] has published a revised table of experimental one-electron term values for free atoms with atomic numbers below 41. Some of these term values show large deviations from those of Landolt-Bornstein which are presented in Figs. 9–12. However, these differences do not essentially affect the qualitative comparisons with the theoretical results.

relativistic hydrogenic energy with an effective Z determined from the uncorrected computed term value. The corrections were always in the proper direction but not sufficiently large to remove the entire discrepancy. The residual error is presumed to arise at least in part from correlation effects.

2. For terms lying below the $3s$-level, the predictions of the Thomas-Fermi-Dirac potential are on the whole closer to the Hartree, or Hartree-Fock, values than are the predictions of the Thomas-Fermi potential. For these terms which lie below the $3s$-level, the Thomas-Fermi-Dirac values agree on the average as well with experiment as do the Hartree values. For terms above the $3s$-level, the Thomas-Fermi values are on the whole closer to the Hartree values than are the Thomas-Fermi-Dirac values; since the experimental ionization values do not vary smoothly for these levels, it may be said that the values from any of the three theoretical possibilities considered here are equally acceptable. It may be remarked that, on a purely empirical basis, an improved overall agreement with experimental values can be obtained by taking the Thomas-Fermi values for atomic number $Z+\frac{1}{2}$ to give the term values for atomic number Z.

3. As can be inferred from the figures, the f series of terms exhibits unusually abrupt alterations in energy. This behavior is observed at the same Z-value for all members of the f-series. For example, at the Z-value for which the $4f$-electron enters the atom, the $5f$- and $6f$-levels simultaneously have a sharp rise in binding energy. This type of behavior for the f-series was predicted by Mayer,[6] who also pointed out the result verified by the present calculations, that the $5f$-term value would take on the $4f$-hydrogenic term value and the $6f$-term value would take on the $5f$-hydrogenic value at the Z-value for which the $4f$-electron enters the atom.

It is to be recognized, of course, that term values alone are not a sensitive test of the accuracy of an effective central field. The uniformity, however, with which the statistical potentials agree with observed binding energies may be taken as indicating that these central fields furnish reasonably good descriptions of atomic behavior. More sensitive tests of these fields consist in the determination of wave functions and matrix elements. For this reason, these wave functions are now being computed and photo-absorption coefficients will then be evaluated. The accuracy of the term

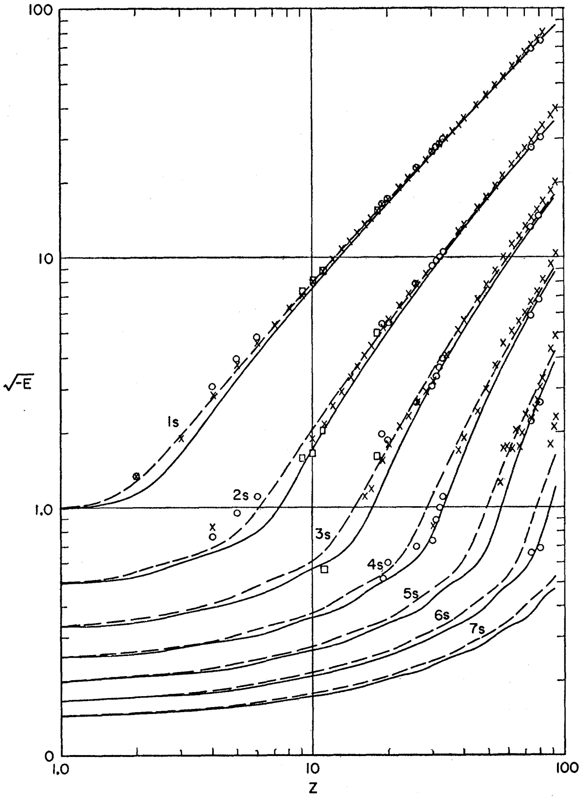

FIG. 9. The square root of the computed s-levels are shown with the solid line for the Thomas-Fermi atom and with the dashed line for the Thomas-Fermi-Dirac atom. The circles (○) are the values computed by the Hartree method; the squares (□) are the values computed by the Hartree-Fock method. The crosses (×) are the experimental values.

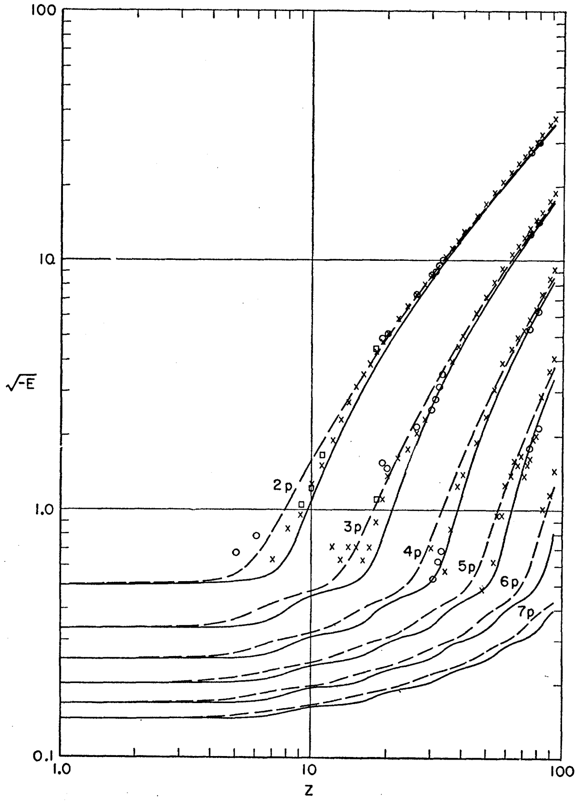

FIG. 10. The square root of the computed p-levels are shown with the solid line for the Thomas-Fermi atom and with the dashed line for the Thomas-Fermi-Dirac atom. The circles (○) are the values computed by the Hartree method; the squares (□) are the values computed by the Hartree-Fock method. The crosses (×) are the experimental values where the doublet energies have been averaged.

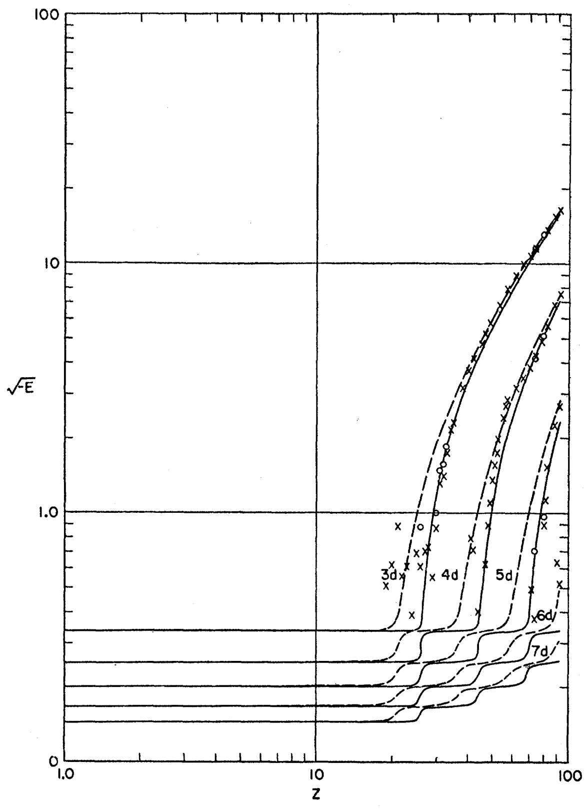

FIG. 11. The square root of the computed *d*-levels are shown with the solid line for the Thomas-Fermi atom and with the dashed line for the Thomas-Fermi-Dirac atom. The circles (○) are the values computed by the Hartree method; the squares (□) are the values computed by the Hartree-Fock method. The crosses (×) are the experimental values where the doublet energies have been averaged.

values for the statistical potentials suggests further that the perturbation expansion will converge rapidly. It may reasonably be expected, therefore, that the first order perturbation correction to the present zero order term values will comprise the principal part of the residual errors. The verification of this conjecture by calculation of the matrix elements of the perturbation operator of Eq. (4) is now in progress.

The statistical model, with the potential that it determines, makes possible the approximate calculation of other kinds of atomic states. For example, the energies and wave functions of ionized atoms may be computed. One may also treat atoms under pressure and atoms at nonzero temperature. For the latter problem, the generalization of the statistical model developed by Feynman, Metropolis, and Teller[19] gives a potential distribution which may be used as an effective central field. This central field approximates the effective field in the atom averaged over the thermal fluctuations of the electron cloud. The term values and one-electron eigenfunctions computed with this potential are averages which neglect the effects of thermal fluctuations. It may be expected that this approach to the effects of temperature on the atom will be particularly useful in computations of opacity and equations of state. These computations are now in progress.

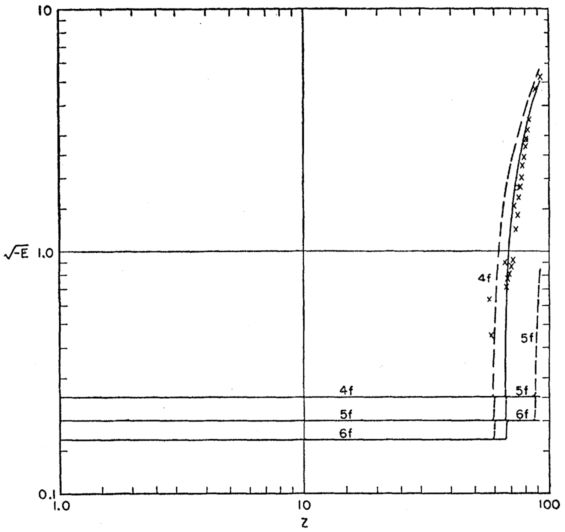

FIG. 12. The square root of the computed *f*-levels are shown with the solid line for the Thomas-Fermi atom and with the dashed line for the Thomas-Fermi-Dirac atom. The circles (○) are the values computed by the Hartree method; the squares (□) are the values computed by the Hartree-Fock method. The crosses (×) are the experimental values where the doublet energies have been averaged.

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[19] Feynman, Metropolis, and Teller, Phys. Rev. **75**, 1561 (1949).