

Whereas, this value is quite small to be interpreted by dissociative recombination, calculation of α_D indicates that collisional-dissociative recombination through a level near $q=4$ could be expected to give an electron-removal rate of

$$\alpha_D = 10^{-11} \text{ cm}^3/\text{sec at } 2000^\circ\text{K.}$$

Consequently, a dissociative state having an energy at the common equilibrium internuclear separation of the bound molecular states comparable to or below that

of the fourth hydrogenic level would yield a collisional-dissociative recombination rate in agreement with that experimentally determined. Since the states with one of the possible Λ values arising from the combination $\text{He}(1^1S) + \text{He}(2^3P)$, the $4p\Sigma$, has not been experimentally located, such a repulsive state with the desired energy could exist. Consequently, at least on the basis of recombination rates, collisional-dissociative recombination offers a promising alternative to dissociative recombination in the explanation of the dissociation observed in decaying helium plasmas.

Binding Energies of Electrons for Modified Thomas-Fermi Potentials

D. SHALITIN

Department of Theoretical Physics, The Hebrew University of Jerusalem, Jerusalem, Israel

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Binding energies of electrons in several neutral atoms are calculated for the Thomas-Fermi, Fermi-Amaldi, and Thomas-Fermi-Dirac models, as well as for three other modified models proposed in this paper. In the modified models the self-interaction of the electrons is explicitly treated. One of these modifications, related to the Fermi-Amaldi model, seems to yield results very close to the experimental values for binding energies above a few tens of eV in atoms with Z up to about 50.

INTRODUCTION

THE Thomas-Fermi^{1,2} (TF) statistical model of the atom is the simplest model which reasonably describes the electrostatic potential and the electron density within the atom. Despite the simplicity and crudeness of the model, one may still use the TF potential to calculate binding energies of electrons by solving a single-particle wave equation. The results of such calculations might *a priori* be considered as a first approximation for calculations on a more refined model of the atom, such as the Hartree or the Hartree-Fock self-consistent method. Often, however, the TF binding energies agree quite well with the experimental values. This agreement improves when the calculations are carried out with the Fermi-Amaldi³ (FA) or the Thomas-Fermi-Dirac⁴ (TFD) potentials.

Extensive calculations of energy *terms* (specified by the n and l quantum numbers) for the TF and TFD models have been carried out by Latter⁵ who solved the Schrödinger equation. In the present work we repeated similar computations for energy *levels* (specified also

by the j quantum number) by solving the Dirac equation. We also computed the energy levels for the FA model and for three modified forms of the above-mentioned models. In these modified models special attention is explicitly paid to the self-energy of each individual electron. It appears that for a rather wide range of elements the binding energies based on one of these models (a modified Fermi-Amaldi model), on the average, agree with the experimental values better than the results based on the more orthodox models. In this respect the results of this particular model may be compared even with the Hartree-Fock results. All three modified models may easily be extended to ions. Two of them (*viz.*, the modified TF and the modified FA models) may also be extended to atoms at finite temperature and pressure, whereas the self-consistent-field methods, although more accurate in principle, are much more difficult to apply to atoms in highly excited states. The two extended models may therefore be used as a basis for calculations of opacity in the interior of stars.

MODIFIED THOMAS-FERMI METHODS

All versions of the TF equation (*i.e.*, TF, FA, and TFD equations) may be obtained from a variational principle

$$E_{\text{pot}} + E_{\text{kin}} = \min, \quad (1)$$

$$\int \rho d^3r = Z, \quad \text{given.} \quad (2)$$

¹ For general reference see P. Gombas, *Die Statistische Theorie Des Atoms* (Springer-Verlag, Berlin, 1949).

² E. Fermi, *Atti Accad. Nazl. Lincei. Rend. Classe sci. fis. mat. e nat.* **6**, 602 (1927); **7**, 342, 726 (1928); L. H. Thomas, *Proc. Cambridge Phil. Soc.* **23**, 542 (1927).

³ E. Fermi and E. Amaldi, *Mem. Acc. Italia* **6**, 117 (1934); see also Ref. 1, p. 65.

⁴ P. A. M. Dirac, *Proc. Cambridge Phil. Soc.* **26**, 376 (1930); see also Ref. 1, p. 77.

⁵ R. Latter, *Phys. Rev.* **99**, 510 (1955).

In all versions the kinetic energy of the electrons E_{kin} has the same form which corresponds to a plane-wave approximation,

$$E_{\text{kin}} = \chi_k \int \rho^{5/3} d^3r; \quad \chi_k = \frac{3}{10} (3\pi^2)^{2/3} e^2 a_0.$$

These versions differ by the particular form chosen for the dependence of the potential energy E_{pot} on the density of the electrons ρ . Using a Lagrange multiplier to account for the extra condition (2), we obtain the basic equation

$$(5/3)\chi_k \rho(r)^{2/3} + \delta E_{\text{pot}}/\delta \rho + eV_0 = 0. \quad (3)$$

$\delta E_{\text{pot}}/\delta \rho$ is the functional derivative of E_{pot} with respect to $\rho(r)$. The following expressions for E_{pot} are used in the various methods:

$$\begin{aligned} E_{\text{pot}} &= -\frac{1}{2}e \int V_e(\mathbf{r})\rho(\mathbf{r})d^3r - Ze^2 \int \frac{\rho(\mathbf{r})}{r} d^3r, & \text{TF} \\ &= -\frac{1}{2} \frac{Z-1}{Z} e \int V_e(\mathbf{r})\rho(\mathbf{r})d^3r - Ze^2 \int \frac{\rho(\mathbf{r})}{r} d^3r, & \text{FA} \quad (4) \\ &= -\frac{1}{2}e \int V_e(\mathbf{r})\rho(\mathbf{r}) - Ze^2 \int \frac{\rho(\mathbf{r})}{r} d^3r + E_{\text{exch}}. & \text{TFD} \end{aligned}$$

Here $V_e(r)$ is the electrostatic potential exerted by all the electrons on an infinitesimal test charge at a point r ,

$$V_e(r) = -e \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r'. \quad (5)$$

E_{exch} is the exchange energy of the atom as a whole. By the plane-wave approximation one deduces

$$E_{\text{exch}} = -\chi_a \int \rho^{4/3} d^3r; \quad \chi_a = \frac{3}{4} (3/\pi)^{1/3} e^2. \quad (6)$$

Inserting the expressions (4) into Eq. (3) we obtain the following relations between the density $\rho(r)$ and the potential $V_e(r)$:

$$\begin{aligned} (5/3)\chi_k \rho^{2/3} - eV_e - Ze^2/r + eV_0 &= 0, & \text{TF} \\ (5/3)\chi_k \rho^{2/3} - e[(Z-1)/Z]V_e - Ze^2/r + eV_0 &= 0, & \text{FA} \quad (7) \\ (5/3)\chi_k \rho^{2/3} - eV_e - Ze^2/r - (4/3)\chi_a \rho^{1/3} + eV_0 &= 0. & \text{TFD} \end{aligned}$$

These relations together with the Poisson equation, obviously obeyed by V_e ,

$$\nabla^2 V_e = 4\pi e \rho \quad (8)$$

yield differential equations for V_e . These differential equations, with auxiliary conditions [Eq. (2), boundness near the nucleus and zero pressure at the edge of the atom], uniquely specify the potential V_e of the free atom for each Z .

The potential V_q which should appear in quantum-

mechanical calculations is the potential actually exerted on an electron of the atom. This potential differs from the potential $V_e + Ze/r$ acting on an infinitesimal test charge because $V_e + Ze/r$ includes the interaction of the charge of electron with itself, and because it does not include exchange effects. One is therefore rather free to choose any of the V_e of Eq. (7) and to correct it by a suitable term accounting for the self-interaction or the exchange potential. The usual potentials V_q used in quantum-mechanical calculations are:

$$\begin{aligned} V_q &= V_{\text{TF}} = V_e + Ze/r \\ &= V_{\text{FA}} = (Z-1)V_e/Z + Ze/r \\ &= V_{\text{TFD}} = V_e + Ze/r + 2\chi_a \rho^{1/3}/e. \end{aligned} \quad (9)$$

The V_e in each version is the potential derived from the corresponding Eq. (7). This choice is natural as it is consistent with the expressions (4) for the energy E_{pot} .

It is obvious that V_{TF} does not approximate the physical potential very well, as it does neither account for the self-energy nor the exchange effects. The only advantage of V_{TF} is that it is more convenient for numerical calculations than the other potentials, because it has a universal form for all atoms.

The FA potential apparently takes into account the self-interaction as appears in the expressions either for E_{pot} and for V_{FA} . However, the expression FA for E_{pot} in Eq. (4) claims only that the self-energy of *all* the electrons is $1/Z$ of their total mutual interaction, which is a rather plausible assumption. The assumption on V_{FA} in Eq. (9) is much more restrictive as it claims that the self-interaction potential exerted on *each* electron is exactly $1/Z$ of the potential exerted on it by all the electrons. This is obviously not valid for electrons not uniformly distributed, as is the case for an actual atom (except for $Z=2$, where the statistical model is naturally not expected to hold).

The TFD potential includes an explicit term of exchange potential $2\chi_a \rho^{1/3}/e$. In a rigorous treatment of exchange effects, the self-interaction is also properly treated (as in the Hartree-Fock method). In the present statistical approximation this is not assured.

We introduce therefore three modified potentials for use in calculations of binding energies of electrons:

$$V_{q \text{ mod}} = V_e + Ze/r - V_{\text{self}}. \quad (10)$$

V_{self} is the potential exerted on a test charge by the electron whose level is calculated, and V_e is again any of the potentials defined in Eq. (7).

More explicit expressions for the potential $V_{q \text{ mod}}$ are

$$\begin{aligned} V_{q \text{ mod}} &= V_{\text{TFM}} = V_{\text{TF}} - V_{\text{self}} \\ &= V_{\text{FAM}} = [Z/(Z-1)](V_{\text{FA}} - e/r) - V_{\text{self}} \\ &= V_{\text{TFDM}} = V_{\text{TFD}} - 2\chi_a \rho^{1/3}/e - V_{\text{self}}. \end{aligned} \quad (10')$$

In these potentials the self-interaction is explicitly taken into account. One is justified in using $V_{q \text{ mod}}$ for

calculations of binding energies, assuming that the major correction to $V_e + Ze/r$ is V_{self} , and that the other corrections due to exchange effects are negligible. These modified potentials and the corresponding models are referred to later as the TFM, FAM, and TFDM potentials and models.

It should be noticed that any of the $V_{q \text{ mod}}$ has some advantage on both the TF and TFD potentials. V_{TF} and V_{TFD} (but not V_{FA}) decrease for large r faster than e/r . It may occur that the number of their bound states are sensibly smaller than Z , whereas all the potentials $V_{q \text{ mod}}$ decrease like e/r for $r \rightarrow \infty$, and therefore have usually more bound states. The modified potentials are also preferable when treating a system consisting of an atom with a hole in an inner shell and an outer electron, having either negative or positive energy. In such systems the potential exerted on the outer electron is a potential of the type $V_{q \text{ mod}}$ and not the TF, FA, or TFD potentials, nor the ion potential related to any of these models. The potential $V_{q \text{ mod}}$ is exactly the model potential of an atom with a hole, provided that the rearrangement effects after creating the hole are negligible. Thus the modified potentials may be of some use, especially for calculations of photoelectric cross sections.

NUMERICAL CALCULATIONS OF BINDING ENERGIES

We solved the Dirac equation in several atoms for electrons whose binding energies are at least of the order of a few tens of eV. The eigenvalues thus obtained for all six potentials defined above are presented in Table I. The eigenvalues, which in our model equal the binding energies, are obtained with an accuracy better than 0.02% by Hartree's method⁶ modified for the Dirac equation.

The TF potential was taken from a table published by Kobayashi *et al.*⁷ which is accurate to the fifth significant figure. The other potentials were calculated by us (see Appendix) with an accuracy better than 0.01%. The differential equations defining the potentials and the wave equation were integrated by the Runge-Kutta-Gill method. All numerical calculations were carried out on a Philco, Transac-2000 computer.

The expressions for the modified potentials, Eq. (10), include a self-potential term $V_{\text{self}}(\mathbf{r})$. This term depends explicitly on the wave function $\Psi(\mathbf{r})$,

$$V_{\text{self}}(\mathbf{r}) = -e \int \frac{\Psi(\mathbf{r}')\Psi^*(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r', \quad (11)$$

and in general is not spherically symmetric. In order to simplify the Dirac equation, V_{self} in expression (11) is

replaced by a spherically symmetric potential

$$V_{\text{self}}(r) = -\frac{e}{r} \int_0^r 4\pi r'^2 [f(r')^2 + g(r')^2] dr' - e \int_r^\infty 4\pi r' [f(r')^2 + g(r')^2] dr', \quad (11')$$

f and g being the two components of Dirac radial wave function.

The Dirac equation with the modified potentials $V_{q \text{ mod}}$, as defined by Eqs. (10) and (11'), is an integro-differential equation. It is solved by iterations: Solving the equation for the potential $V_e + Ze/r$, one obtains the eigenvalue ϵ^0 and the eigenfunction Ψ^0 . The self-potential V_{self}^0 corresponding to Ψ^0 is evaluated and, solving the equation again for $V_e + Ze/r - V_{\text{self}}^0$, one obtains a new eigenvalue ϵ^1 and a new eigenfunction Ψ^1 . With the new function Ψ^1 the self-potential V_{self}^1 is calculated, and so on.

This method converges very rapidly. The difference $\epsilon^2 - \epsilon^1$ is of the order of a few eV (usually less than 4eV), and $\epsilon^3 - \epsilon^2$ is usually less than 0.5 eV. The equality of the eigenfunctions is also remarkable: In most cases the ratio $(\Psi^2 - \Psi^1)/\Psi^2$ is less than 0.5% for the main part of the function. In fact the eigenvalues for the modified potentials presented in Table I are those obtained after a single iteration (i.e., ϵ^1). Only when the binding energy is low, say a few tens of eV, the eigenvalues ϵ^2 , obtained after a second iteration, are given. In the table the eigenvalues for all six potentials discussed above are given along with the most recent experimental binding energies available to the author.^{8,9}

DISCUSSION OF THE RESULTS

The binding energies of the pure TF model reveal the following features: Almost all the calculated binding energies ϵ_{cal} are lower than the experimental values ϵ_{exp} . For a certain level (e.g., $1s\frac{1}{2}$) and different values of Z 's, the difference $\epsilon_{\text{exp}} - \epsilon_{\text{cal}}$ grows roughly proportionally to Z until $Z \approx 60$, although the ratio $(\epsilon_{\text{exp}} - \epsilon_{\text{cal}})/\epsilon_{\text{exp}}$ decreases like $1/Z$. For atomic numbers greater than 60 the differences themselves decrease, becoming negligibly small for $Z \approx 82$, or may even change sign (e.g., for $Z=92$, K and L electrons).

The explanation is probably the following: As mentioned above, the TF model includes self-interaction and neglects the exchange energy, both affecting to lower the binding energies. On the other hand, this model, and all the other models mentioned in the present work, are not relativistic. The neglect of relativistic effects reduces the calculated screening of the nuclear

⁶ D. R. Hartree, *The Calculation of Atomic Structure* (John Wiley & Sons, Inc., New York, 1957).

⁷ S. Kobayashi, T. Matsukuma, S. Nogai, and K. Umeda, J. Phys. Soc. Japan 10, 759 (1955).

⁸ *Alpha, Beta and Gamma Ray Spectroscopy*, edited by K. Siegbahn (North-Holland Publishing Company, Amsterdam, 1965), Vol. I, p. 852.

⁹ A. Fahlman, K. Hamrin, R. Nordberg, C. Nordling, and K. Siegbahn, Phys. Rev. Letters 14, 127 (1965). From this reference the experimental $2s$ energies for atomic numbers 8, 12, and 13 are cited in Table I.

potential, specifically near the nucleus, and increases the calculated binding energies. This increase in binding energies is negligible for low Z 's but grows rapidly for higher Z 's; for very high Z 's it may become comparable to or even greater than the decrease in binding energy due to the self-interaction and the neglect of exchange effects. This relativistic effect is most pronounced for the inner shells. We limit therefore, momentarily, our

discussion to atomic numbers up to 50, where the relativistic effects are not yet pronounced.

The TFM binding energies are, of course, always higher than the TF values, and are almost always higher than the experimental ones. However, they are nearer to the experimental values than the TF results, for all but the most loosely bound levels.

The FA binding energies are almost always better

TABLE I. Energy levels in eV for six statistical models.

Z	Level	Experimental Refs. 8 and 9	TF	TFM	FA	FAM	TFD	TFDM
2	$1s_{1/2}$	24.6	10.4	33.9	26.4	26.4	25.1	29.3
4	$1s_{1/2}$	112	77	135	99	117	113	118
6	$1s_{1/2}$	284	221	312	247	290	280	288
8	$1s_{1/2}$	532	448	573	479	547	532	543
	$2s_{1/2}$	23.7	17	34	27	24.4	32	22.5
10	$1s_{1/2}$	867	764	922	798	894	874	887
12	$1s_{1/2}$	1305	1171	1364	1209	1333	1308	1323
	$2s_{1/2}$	89.2	73	108	87	89.6	103	86
	$2p_{1/2}$	52	41	77	56	56	74	53
	$2p_{3/2}$		41	77	55	56	74	53
13	$1s_{1/2}$	1560	1411	1620	1450	1588	1560	1576
	$2s_{1/2}$	117	95	134	110	113	129	110
	$2p_{1/2}$	73	58	98	73	76	93	72
	$2p_{3/2}$		58	98	73	76	93	72
26	$1s_{1/2}$	7112	6752	7186	6808	7144	7087	7110
	$2s_{1/2}$	842	750	841	776	806	845	789
	$2p_{1/2}$	721	634	739	663	703	738	683
	$2p_{3/2}$	709	623	726	651	691	725	672
	$3s_{1/2}$	94	80	109	91	89	109	83
	$3p_{1/2}$	54	48	75	58	55	75	50
	$3p_{3/2}$		47	75	58	55	75	50
37	$1s_{1/2}$	15 200	14 721	15 354	14 789	15 305	15 224	15 255
	$2s_{1/2}$	2065	1943	2079	1977	2039	2100	2007
	$2p_{3/2}$	1805	1693	1850	1730	1807	1860	1774
	$3s_{1/2}$	322	294	342	310	313	349	298
	$3p_{3/2}$	238	219	266	235	237	273	223
	$3d_{5/2}$	110	103	150	118	121	154	106
	$4s_{1/2}$	29	27	44	34	29	43	25
50	$1s_{1/2}$	29 200	28 611	29 492	28 690	29 436	29 324	29 369
	$2s_{1/2}$	4465	4272	4467	4315	4419	4512	4372
	$2p_{1/2}$	4156	3979	4212	4027	4163	4242	4112
	$2p_{3/2}$	3929	3755	3977	3801	3927	4005	3878
	$3s_{1/2}$	884	802	874	824	837	895	811
	$3p_{1/2}$	757	686	760	708	722	782	695
	$3p_{3/2}$	715	645	716	667	680	737	653
	$3d_{3/2}$	493	440	518	463	481	534	452
	$3d_{5/2}$	485	432	510	455	472	524	443
	$4s_{1/2}$	137	118	147	128	125	151	114
	$4p_{1/2}$	88	81	108	90	86	112	76
	$4p_{3/2}$		74	102	90	86	103	70
56	$1s_{1/2}$	37 441	36 806	37 809	36 890	37 752	37 622	37 674
	$2s_{1/2}$	5987	5736	5960	5783	5909	6017	5854
	$2p_{3/2}$	5247	5019	5271	5069	5219	5309	5162
	$3s_{1/2}$	1293	1152	1235	1176	1196	1265	1163
	$3p_{3/2}$	1061	938	1021	962	981	1050	948
	$3d_{5/2}$	774	673	765	699	723	786	689
	$4s_{1/2}$	259	194	229	205	203	236	188
	$4p_{3/2}$	176	130	163	141	138	170	125
	$4d_{5/2}$	91	49	76	58	54	82	42
60	$1s_{1/2}$	43 569	42 947	44 033	43 034	43 976	43 834	43 894
	$2s_{1/2}$	7126	6865	7109	6915	7057	7176	6997
	$2p_{3/2}$	6208	5976	6249	6029	6195	6293	6133
	$3s_{1/2}$	1575	1432	1524	1458	1482	1559	1445
	$3p_{3/2}$	1294	1170	1261	1197	1219	1295	1183
	$3d_{5/2}$	979	868	969	896	926	995	886
	$4s_{1/2}$	316	259	298	271	270	309	253
	$4p_{3/2}$	225	180	216	192	189	225	173
	$4d_{5/2}$	118	80	113	91	87	120	73
	$5s_{1/2}$	38	26	42	32	28	42	23

TABLE I (continued).

Z	Level	Experimental Refs. 8 and 9	TF	TFM	FA	FAM	TFD	TFDM	
70	1s _{1/2}	61 332	60 879	62 191	60 974	62 130	61 952	62 035	
	2s _{1/2}	10 488	10 294	10 591	10 350	10 535	10 683	10 462	
	2p _{3/2}	8943	8785	9110	8843	9053	9172	8978	
	3s _{1/2}	2398	2320	2432	2350	2386	2484	2338	
	3p _{3/2}	1951	1891	2002	1922	1956	2051	1909	
	3d _{5/2}	1528	1482	1606	1515	1558	1645	1509	
	4s _{1/2}	487	484	533	499	500	552	475	
	4p _{3/2}	345	350	396	364	365	413	341	
	4d _{5/2}	186	200	244	214	213	259	191	
	5s _{1/2}	55	67	89	75	70	92	46	
	82	1s _{1/2}	88 006	87 937	89 556	88 042	89 494	89 258	89 383
		2s _{1/2}	15 860	15 764	16 133	15 828	16 073	16 266	15 985
		2p _{1/2}	15 198	15 171	15 627	15 241	15 564	15 719	15 472
		2p _{3/2}	13 035	12 975	13 365	13 040	13 303	13 449	13 215
3s _{1/2}		3850	3807	3947	3843	3895	4024	3836	
3p _{1/2}		3554	3531	3680	3569	3628	3761	3565	
3p _{3/2}		3066	3043	3178	3078	3127	3248	3068	
3d _{3/2}		2586	2578	2736	2617	2682	2794	2619	
3d _{5/2}		2484	2474	2627	2512	2573	2682	2511	
4s _{1/2}		902	897	961	916	923	993	887	
4p _{1/2}		770	777	841	796	802	874	766	
4p _{3/2}		647	656	714	673	677	743	644	
4d _{3/2}		444	457	515	474	478	542	444	
4d _{5/2}		422	434	491	451	454	519	421	
4f _{5/2}		146	174	231	191	194	250	162	
4f _{7/2}		140	169	226	185	189	243	157	
5s _{1/2}		156	161	190	170	166	198	150	
5p _{1/2}		113	118	146	127	122	124	107	
5p _{3/2}		94	93	118	101	97	121	83	
92		1s _{1/2}	115 603	116 111	118 030	116 226	117 969	117 665	117 846
		2s _{1/2}	21 756	21 772	22 211	21 843	22 148	22 371	22 048
	2p _{1/2}	20 947	21 062	21 612	21 139	21 547	21 729	21 441	
	2p _{3/2}	17 167	17 190	17 635	17 260	17 571	17 740	17 470	
	3s _{1/2}	5549	5497	5664	5538	5608	5764	5537	
	3p _{1/2}	5181	5158	5337	5202	5280	5443	5206	
	3d _{3/2}	3728	3710	3894	3753	3837	3970	3762	
	4s _{1/2}	1441	1400	1477	1423	1434	1522	1390	
	4p _{1/2}	1273	1245	1322	1268	1279	1370	1234	
	4d _{3/2}	780	757	827	778	786	865	743	
	4f _{5/2}	387	378	450	399	408	478	366	
	5s _{1/2}	322	291	328	302	299	342	276	
	5p _{1/2}	260	230	265	241	237	280	216	
	5d _{3/2}	106	85	113	94	89	122	72	

than the pure TF values. Nevertheless they are also usually lower than the experimental values and agree with experiment less than the TFM values for the low-lying levels.

The FAM model is the most consistent in treating the self-interaction, and indeed yields binding energies which, on the whole, agree very well with the experiment. In fact its values deviate from experimental values only rarely by more than 5% and never more than 10%. The binding energies of the K electrons in this model are always a little higher than the experimental values, whereas all the rest are usually slightly lower.

The TFD binding energies are almost always higher than the experimental values. For the K shell they are very good especially for low Z. For other shells the TFD values agree quite well with the experimental values; only for loosely bound levels they deviate considerably.

The TFDM values agree usually quite well with experiment, although a little worse than the TFD

results. However, for the most loosely bound levels they agree better than the TFD values. The binding energies obtained by the TFDM model for K-shell electrons are usually higher than the experimental or the TFD values, but for the other shells they are usually lower.

For atomic numbers between 55 and 80, the range in which relativistic effects begin to be pronounced, no potential among the six is predominantly better than the others. For Z's higher than 80 the models which yield the lowest results, namely the TF, FA, and TFDM models, agree quite well with experiment.

For all the potentials the level splitting within any term is very near to the experimental splitting as may be seen in Table I for Z=26, 50, 82. Thus for several atoms only one level of each term is evaluated and tabulated.

COMPARISON WITH A PREVIOUS CALCULATION

Latter⁵ has carried out extensive calculations of electron energy terms for both the TF and the TFD

TABLE II. Comparison between relativistic self-consistent Liberman-Waber-Cromer (LWC) and FAM binding energies for $Z=26$. Values are given in eV.

Level	Experimental Ref. 8	LWC Ref. 10	FAM
$1s_{1/2}$	7112	7081	7144
$2s_{1/2}$	842	843	806
$2p_{1/2}$	721	733	703
$2p_{3/2}$	709	720	691
$3s_{1/2}$	94	101	89
$3p_{1/2}$	54	68	55
$3p_{3/2}$		66	55

models. His calculation differs however from the present in some respects: (a) Latter has solved a Schrödinger, instead of a Dirac equation. (b) His potentials were not the exact TF and TFD potentials but some analytical approximations which were probably not good enough, especially for the TFD potentials. (c) Latter has slightly modified the potentials for large r , a rather arbitrary modification which implies discontinuity of the electrostatic field. Consequently, Latter's results are very far from either the experimental or our results for high Z 's and inner shells. For low Z 's his TF values nearly coincide with the results presented here, but there is a relatively large discrepancy between his TFD results and ours, the latter being nearer to the experimental values. Also, as Latter bases his calculations on the Schrödinger equation without spin-orbit interaction, he obtains only term values (i.e., each value corresponds to a weighted mean of energy levels belonging to the same term). In the present calculations, based on the Dirac equation, level rather than term values are naturally evaluated.

CONCLUSIONS

As a working model for calculating binding energies the TF model is satisfactory for high atomic numbers ($Z > 80$). For Z up to 50 the FAM, TFD, and TFDM binding energies are much better than the TF values. The TFD energies agree very well with the experimental values for K -shell electrons, especially for low Z (even for $Z=2$), which is quite unexpected of a statistical model. On the average, however, the results yielded by the FAM model are probably the best. They may sometimes even compete with results obtained by the relativistic Hartree-Fock method,¹⁰ as is shown in Table II for $Z=26$. The FAM model has also the following desirable characteristics: (a) It is relatively easy to extend the model to ions and to atoms at finite temperature and pressure, as has already been done¹¹ for the TF potential (such an extension is more difficult

¹⁰ D. Liberman, J. T. Waber, and D. T. Cromer, Phys. Rev. **137**, A27 (1965). In fact the calculations in this reference are not strictly according to the Hartree-Fock method: The exchange term in the self-consistent potential is replaced by $2\chi_{\alpha}\rho^{1/2}/e$.

¹¹ R. P. Feynman, N. Metropolis, and E. Teller, Phys. Rev. **75**, 1561 (1949), R. Latter, *ibid.* **99**, 1854 (1955).

for the TFD and TFDM models). (b) The potential appearing in the Dirac equation may be consistently applied to calculations of photoelectric cross sections (this is true also for the TFM and the TFDM models). (c) The density of the electrons according to the model is continuous (as opposed to the density implied by the TFD and TFDM models).

It should be noticed that no potential among the six discussed in this work fits in the whole range of the intermediate elements (Z between 55 and 80). An abnormal feature in this range is the fact that the TFM binding energies for atomic numbers 56 and 60 are usually lower than the experimental values. This is perhaps due to lack of precision of the experimental data.

It is not being claimed that any of the potentials discussed in the present paper is in principle better than the others. It has only been shown that a certain potential yields better binding energies for a certain range of elements. No attempt has been made here to include relativistic, kinetic-energy, or correlation effects. Taking into account some or all of these effects one may obtain more refined statistical models of the atom. Calculations with such models might possibly yield better results for still wider ranges of elements.

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APPENDIX: EVALUATION OF THE FA AND TFD POTENTIALS

A. FA Potential

The Fermi-Amaldi equation for the potential V_{FA} in a free atom is³

$$d^2\Phi/dx^2 = \Phi^{3/2}/x^{1/2} \quad (A1)$$

with the boundary conditions

$$\Phi(0) = 1, \quad \Phi(x_0) = 0, \quad x_0\Phi'(x_0) = -1/Z, \quad (A2)$$

where

$$\Phi(x) = r(V_{FA} - e/r_0)/Ze, \\ x = [128(Z-1)^2/9\pi^2Z]^{1/3}r/a_0,$$

r_0 , the finite radius of the atom.

Equations (A1)-(A2) transform by $x = x_0\xi$, $\Phi = \Psi/Z$ to the equations

$$d^2\Psi/d\xi^2 = \alpha\Psi^{3/2}/\xi^{1/2}, \quad (A3)$$

TABLE III. α versus Z for the FA potential.

α	Z
3.58609	2
7.13143	4
9.11885	6
11.49331	10
12.64957	13
15.48307	26
16.79995	37
17.85750	50
18.46871	60
18.96863	70
19.46596	82
19.81775	92
20.06754	100

TABLE IV. α versus Z for the TFD potential.

α	Z
0.744985	2
0.900228	4
0.992521	6
1.108271	10
1.166902	13
1.317107	26
1.390145	37
1.450309	50
1.485697	60
1.514980	70
1.544412	82
1.565414	92
1.580417	100

with the boundary conditions

$$\Psi(0)=Z, \quad \Psi(1)=0, \quad \Psi'(1)=-1, \quad (A4)$$

where

$$\alpha=(X_0^3/Z)^{1/2}.$$

The equation is singular at the origin, and it is more convenient to solve it inwardly. With some chosen value α , the equation is integrated up to some small ξ and then Ψ is extrapolated for $\xi=0$ by a third-order polynomial in $\xi^{1/2}$. The value $Z=\Psi(0)$ thus calculated, together with α determine $\Phi(x)$, and therefore also $V_{FA}(r)$ and the corresponding $V_e(r)$ for this Z . This method is very stable, and for a specified α yields results with an accuracy better than 0.01% for Z and V_e . It is found that α is nearly linear with $\ln Z$. Having a table of $\ln Z$ versus α , we calculated V_{FA} for any required Z by interpolating α as a third-order polynomial of $\ln Z$ and integrating Eqs. (A3)–(A4) with this interpolated α . The difference between Z thus calculated and the required Z is nowhere more than 10^{-4} . In Table III some values of α with the corresponding Z are listed.

B. TFD Potential

The TFD equation for the potential V_{TFD} in a free atom is⁴

$$d^2\Phi/dx^2=x[(\Phi/x)^{1/2}+\beta_0]^3 \quad (A5)$$

with the boundary conditions of Jensen¹²

$$\Phi(0)=1, \quad \Phi(x_0)=x_0\beta_0^2/16, \quad x_0\Phi'(x_0)=\Phi(x_0), \quad (A6)$$

where

$$\Phi(x)=r[V_e(r)+Ze/r-e/32\pi^2a_0]/Ze,$$

$$x=r/\mu; \quad \mu=(9\pi^2/128Z)^{1/3}a_0,$$

$$\beta_0=(3/32\pi^2Z^2)^{1/3},$$

$$r_0=\mu x_0, \quad \text{the finite radius of the atom.}$$

Equations (A5)–(A6) transform by $x=x_0\xi$, $\Phi=b\Psi$ (b is yet unknown) to the equations

$$d^2\Psi/d\xi^2=\alpha\xi[(\Psi/\xi)^{1/2}+\gamma]^3 \quad (A7)$$

with the boundary conditions

$$\Psi(0)=1/b, \quad \Psi(1)=\gamma^2/16, \quad \Psi'(1)=\Psi(1), \quad (A8)$$

where

$$\alpha=(x_0^3b)^{1/2}, \quad \gamma=(x_0/b)^{1/2}\beta_0.$$

With $\Psi(1)=1$ (and therefore $\gamma=4$) and some chosen α , Eqs. (A7)–(A8) are integrated as in the case of the V_{FA} potential.

The value $\Psi(0)$ together with α determine Z and $\Phi(x)$, and therefore also the potentials $V_e(r)$ and $V_{TFD}(r)$. In Table IV some values of α with the corresponding Z are listed.

¹² H. Jensen, Z. Physik **93**, 232 (1935). See also Ref. 1, p. 79.