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Binding Energies of Electrons in Positive Ions for Statistical Potentials

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Binding energies of electrons in several positive ions of some light elements and of iron are calculated for six statistical models. The models discussed are the Thomas-Fermi, Fermi-Amaldi, and Thomas-Fermi-Dirac models and three other modified models, in which the self-interaction of the electrons is explicitly treated.

INTRODUCTION

In a recent work,[1] energy levels of electrons in several neutral atoms have been computed for six statistical models. These models were the Thomas-Fermi (TF), Fermi-Amaldi (FA), and Thomas-Fermi-Dirac (TFD) models and three modifications which were denoted by TFM, FAM, and TFDM. In the modified models, special attention was paid to the self-interaction of each individual electron. The agreement of the calculated energies with the experimental values was found to be reasonably good for not too heavy elements (especially for the FAM and the TFD models).

In the present paper, similar calculations are repeated for some positive ions in their ground state: some light elements (from $Z=3$ to $Z=13$) in several degrees of ionization and several iron ions. Unfortunately, hardly any measurement is available for these binding energies, and direct comparison with experimental results is practically impossible. This is due to difficulties of experimenting with highly-ionized atoms in terrestrial laboratories. However, these ions may exist as free long-lived ions in stellar atomspheres or the solar corona. Although we should assume high temperatures for a rigorous treatment of these astrophysical ions, it is hoped that the zero-temperature binding energies, as calculated in the present work, may be regarded as a plausible approximation to the actual values.

EVALUATION OF THE POTENTIALS

The potentials V_q or $V_{q\,\mathrm{mod}}$ acting on an electron within an ion are, according to the various models[1,2]

$$\begin{aligned} V_q &= V_{\mathrm{TF}} = V_e + Ze/r \\ &= V_{\mathrm{FA}} = [(N-1)V_e/N] + Ze/r \\ &= V_{\mathrm{TFD}} = V_e + Ze/r + 2\chi_a\rho^{1/3}/e. \end{aligned} \tag{1}$$

$$\begin{aligned} V_{q\,\mathrm{mod}} &= V_e + Ze/r - V_{\mathrm{self}} \\ &= V_{\mathrm{TFM}} = V_{\mathrm{TF}} - V_{\mathrm{self}} \\ &= V_{\mathrm{FAM}} = (NV_{\mathrm{FA}} - Ze/r)/(N-1) - V_{\mathrm{self}} \\ &= V_{\mathrm{TFDM}} = V_{\mathrm{TFD}} - 2\chi_a\rho^{1/3}/e - V_{\mathrm{self}}. \end{aligned} \tag{1'}$$

Here V_e is the electrostatic potential produced by *all* the electrons of the ion and acting on a test charge; V_{self} is the electrostatic potential produced by the electron whose level is calculated; ρ is the electron density; Z is the atomic number of the ion; N is the number of electrons in the ion; and $\chi_a = \frac{3}{4}(3/\pi)^{1/3}e^2$.

The differential equation for the potentials V_{TF} and V_{FA} of a free ion is[3]

$$d^2\Phi/dx^2 = \Phi^{3/2}/x^{1/2}, \tag{2}$$

with the boundary conditions

$$\Phi(0)=1, \quad \Phi(x_0)=0, \quad x_0\Phi'(x_0) = -q/Z, \tag{3}$$

where

$$\Phi(x) = r(V_q - eq/r_0)/Ze,$$
$$x = r/\mu,$$
$$\left.\begin{aligned} \mu &= \mu_0 = (9\pi^2/128Z)^{1/3}a_0 \\ q &= Z-N \end{aligned}\right. \quad \text{for TF},$$

and

$$\left.\begin{aligned} \mu &= \mu_0(N/N-1)^{2/3} \\ q &= Z-N+1 \end{aligned}\right. \quad \text{for FA}.$$

The solutions of this differential equation form a family of functions whose only parameter Z/q is always positive for positive ions. Equations (2) and (3) are singular at the origin, and hence it is more convenient to solve them inwardly. For this purpose we transform them by $x = x_0\xi$, $\Phi = q\Psi/Z$ to the equations

$$d^2\Psi/d\xi^2 = \alpha\Psi^{3/2}/\xi^{1/2}, \tag{2'}$$

with the boundary conditions

$$\Psi(0) = Z/q, \quad \Psi(1) = 0, \quad \Psi'(1) = -1. \tag{3'}$$

The only parameter for these equations is $\alpha = (qx_0^3/Z)^{1/2}$, and its functional dependence on Z/q is just like the dependence of α on Z in Table III of Ref. 1 This table may be used for interpolation, also for the solutions of Eqs. (2′) and (3′).

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[1] D. Shalitin, Phys. Rev. **140**, A1857 (1965).

[2] The potentials V_q are not necessarily purely electrostatical. Specifically, V_{TFD} contains a term $2\chi_a\rho^{1/3}/e$, which is Slater's average exchange potential within the ion. See, e.g., J. C. Slater, Phys. Rev. **81**, 385 (1951), Eq. (13).

[3] P. Gombas, *Die Statistische Theorie Des Atoms und Ihre Anwendungen* (Julius Springer-Verlag, Vienna, 1949), p. 30 ff. and p. 65 ff.

TABLE I. α versus Z and p for the TFD potential.

$p \backslash Z$	4	6	10	13	26	50	82	100
1	0.281478	0.375851	0.495636	0.556705	0.713889	0.853790	0.952765	0.990649
2	0.104286	0.180824	0.283047	0.336668	0.477995	0.606761	0.699120	0.734701
3		0.089580	0.175634	0.221941	0.347916	0.465489	0.550977	0.584121
4		0.040616	0.112045	0.152563	0.265254	0.372988	0.452351	0.483304
5			0.071667	0.106973	0.208267	0.307492	0.381511	0.410544
6			0.044653	0.075393	0.166821	0.258656	0.328005	0.355352
7				0.052737	0.135510	0.220870	0.286108	0.311967
8				0.036100	0.111176	0.190807	0.252397	0.276931
9					0.091843	0.166363	0.224687	0.248034
10					0.076216	0.146135	0.201516	0.223791

The equation for the TFD potential in a free ion is[4,5]

$$d^2\Phi/dx^2 = x[(\Phi/x)^{1/2} + \beta_0]^3, \tag{4}$$

with the boundary conditions

$$\Phi(0) = 1, \quad \Phi(x_0) = \beta_0{}^2 x_0, \quad x_0\Phi'(x_0) - \Phi(x_0) = -p/Z. \tag{5}$$

Here

$$\Phi = r(V_e + Ze/r - pe/r_0 + e/32\pi^2 a_0)/Ze; \quad \beta_0 = (3/32\pi^2 Z^2)^{1/3};$$

$x = r/\mu_0$; $r_0 = \mu_0 x_0$, the finite radius of the ion; and $p = Z - N$, the degree of ionization. The solutions of Eqs. (4) and (5) form a two-parameter family. A convenient way to solve them is by the transformation $x = x_0\xi$, $\Phi = b\Psi$ (where b is yet unknown). The new equations are

$$d^2\Psi/d\xi^2 = \alpha\xi[(\Psi/\xi)^{1/2} + \gamma]^3, \tag{4$'$}$$

with the boundary conditions

$$\Psi(0) = 1/b, \quad \Psi(1) = \tfrac{1}{16}\gamma^2, \quad \Psi'(1) = \Psi(1) - p/Zb, \tag{5$'$}$$

where

$$\alpha = (x_0{}^3 b)^{1/2}, \quad \gamma = (x_0/b)^{1/2}\,\beta_0 = (9x_0{}^3/1024\pi^4 b^3 Z^4)^{1/6}.$$

With $\Psi(1) = 1$ (and $\gamma = 4$) and some chosen α, Zb is specified $[Zb = (3\alpha/32\pi^2\gamma^3)^{1/2}]$. Thus, with α, $\Psi(1)$, and $\Psi'(1)$ specified, Eqs. (4′) and (5′) may be integrated up to a small ξ and then interpolated for $\xi = 0$. With the value $1/b = \Psi(0)$, Ψ and V_{TFD} may be calculated. It is found that for a fixed p, α is nearly linear with $\ln(Z-p)$. In Table I some values of α with the corresponding Z and p are listed.

RESULTS AND DISCUSSION

The binding energies have been calculated as eigenvalues of the Dirac equation with the six potentials and are presented in Table II. The method of calculation is described in Ref. 1. All but some of the most loosely bound levels were computed. Because the only experimental binding energies known to the author are for the external electrons[6] ('ionization potential') the comparison between theory and experiment is necessarily sporadic. The six sets of results should therefore be regarded as six sets of predictions, none of which may as yet be preferred to the others. Only in the future, when more measurements are carried out, will it be decided which of the models is the best. However, with the present experimental data, it seems that only rarely do the FAM or the TFDM models yield the best results. On the other hand, it seems that frequently the FA and, especially for the heavier ions, the TFD values are nearest to experiment. It also occurs frequently that the experimental values fit better to the last but one occupied term in the ion.

An interesting feature of the theoretical results is the constancy of the level splitting within any term: For a given element and a given term, it has nearly the same value for all the ions and even for all the potentials. For the heavier ions ($Z = 13, 26$), a more general feature is revealed: When we pass from a certain ion of an element to the following ion, all the levels are shifted practically by the same amount, which depends on the ion and slightly on the potential. This is consistent with a naive model of an ion consisting of classical electron shells, but it is also quite consistent with the usual shell model. Like the results for neutral atoms, the TF values are nearly always the lowest and the TFM or the TFD are usually the highest. The FAM and TFDM values are often very close, and for most ions and all shells, except the K shell, the FA values are also rather close to them. The TFD binding energies, although relatively good for the heavier ions (and very good for the K shell electrons in low-Z *atoms*[1]), exhibit some irregularities for the $2s_{1/2}$ level in carbon and oxygen ions. This fact is not a major defect for a statistical model, yet it sheds some doubts on the reliability of this model when applied to ions with a very small number of electrons.

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[4] Ref. 3, p. 77 ff.

[5] In Ref. 1, the definition of $\Phi(x)$ is misprinted. The equation following Eq. (A6) there should read $\Phi(x) = r[V_e(r) + Ze/r + e/32\pi^2 a_0]/Ze$. The error does not appear in the corresponding computer program and does not affect the validity of the TFD or TFDM results in Table I of Ref. 1.

[6] *Atomic Energy Levels*, edited by C. E. Moore, Natl. Bur. Std. (U. S.) Circ. No 467 (U. S. Government Printing and Publishing Office, Washington, D. C., 1949, 1952), Vols. 1 and 2.

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

Z	p	level	TF	TFM	FA	FAM	TFD	TFDM	Experimental (Ref. 4)
3	1	$1s_{1/2}$	44	85	78	75	73	78	76
4	1	$1s_{1/2}$	85	143	120	130	126	131	
	2	$1s_{1/2}$	105	164	156	154	149	157	154
6	1	$1s_{1/2}$	228	319	265	300	291	300	
		$2s_{1/2}$	11	25	26	20	22	20	
	2	$1s_{1/2}$	244	335	293	319	311	320	
		$2s_{1/2}$	24	38	43	36	29	36	48
	3	$1s_{1/2}$	270	361	334	349	341	350	
		$2s_{1/2}$	41	58	64	57	27	57	64
8	1	$1s_{1/2}$	455	579	495	557	543	554	
		$2s_{1/2}$	23	43	40	34	42	34	
		$2p_{1/2}$	10	29	25	19	26	19	
		$2p_{3/2}$	10	29	25	19	26	19	35
	2	$1s_{1/2}$	468	593	518	573	560	571	
		$2s_{1/2}$	36	56	57	50	56	50	
		$2p_{1/2}$	22	42	42	36	40	36	55
	3	$1s_{1/2}$	490	614	552	597	585	596	
		$2s_{1/2}$	53	75	79	71	71	72	
		$2p_{1/2}$	39	60	65	56	56	56	77
	4	$1s_{1/2}$	521	646	596	631	619	631	
		$2s_{1/2}$	76	99	106	97	83	97	114
	5	$1s_{1/2}$	564	689	658	677	665	679	
		$2s_{1/2}$	103	128	138	127	83	127	138
10	1	$1s_{1/2}$	770	929	813	903	884	897	
		$2s_{1/2}$	45	72	63	60	71	59	
		$2p$	23	51	41	37	48	36	41
	2	$1s_{1/2}$	783	941	834	918	900	913	
		$2s_{1/2}$	57	84	80	75	86	74	
		$2p$	35	63	58	53	63	52	64
	3	$1s_{1/2}$	802	960	863	939	922	935	
		$2s_{1/2}$	74	102	102	95	104	95	
		$2p$	52	79	80	71	81	71	97
	4	$1s_{1/2}$	828	986	900	967	951	965	
		$2s_{1/2}$	96	125	128	120	126	120	
		$2p_{1/2}$	74	103	107	97	103	97	126
	5	$1s_{1/2}$	862	1021	948	1004	989	1003	
		$2s_{1/2}$	124	153	160	150	147	150	
		$2p_{1/2}$	101	133	139	129	128	129	158
13	1	$1s_{1/2}$	1416	1626	1463	1597	1570	1585	
		$2s_{1/2}$	101	140	122	123	139	120	
		$2p$	64	104	85	86	102	82	
	2	$1s_{1/2}$	1428	1637	1482	1610	1584	1600	
		$2s_{1/2}$	112	151	136	136	153	134	
		$2p$	75	115	101	100	116	97	
	3	$1s_{1/2}$	1444	1652	1507	1628	1604	1620	
		$2s_{1/2}$	128	167	158	155	171	153	
		$2p$	91	132	122	118	135	116	120
	4	$1s_{1/2}$	1466	1675	1538	1652	1629	1644	
		$2s_{1/2}$	149	188	183	178	194	176	
		$2p$	111	153	147	141	158	140	154
	5	$1s_{1/2}$	1494	1704	1576	1681	1660	1676	
		$2s_{1/2}$	174	213	213	206	221	205	
		$2p$	137	179	177	170	185	169	190
	6	$1s_{1/2}$	1530	1739	1622	1718	1698	1714	
		$2s_{1/2}$	204	244	248	239	251	238	
		$2p$	168	211	213	203	216	203	242
	7	$1s_{1/2}$	1573	1783	1679	1764	1745	1762	
		$2s_{1/2}$	240	281	288	277	286	276	
		$2p_{1/2}$	204	249	252	243	251	243	285
26	1	$1s_{1/2}$	6757	7191	6819	7151	7095	7119	
		$2s_{1/2}$	755	845	786	814	854	798	
		$2p_{1/2}$	639	743	673	711	746	693	
		$2p_{3/2}$	628	731	661	698	733	680	
26	1	$3s_{1/2}$	85	114	100	97	117	91	
		$3p_{1/2}$	53	80	68	64	84	59	
	2	$1s_{1/2}$	6767	7200	6834	7162	7107	7131	
		$2s_{1/2}$	764	854	799	826	866	810	
		$2p_{1/2}$	648	753	686	722	758	704	
		$2p_{3/2}$	637	740	674	711	745	692	
		$3s_{1/2}$	94	123	112	108	129	103	
		$3p_{1/2}$	63	90	80	75	96	70	
		$3p_{3/2}$	61	88	79	74	94	69	
	3	$1s_{1/2}$	6779	7213	6852	7176	7122	7146	
		$2s_{1/2}$	777	867	815	840	881	825	
		$2p_{1/2}$	661	765	703	736	774	720	
		$2p_{3/2}$	650	752	691	724	761	707	
		$3s_{1/2}$	106	135	127	123	143	118	
		$3p_{1/2}$	75	102	95	90	110	85	
		$3d$	25	47	43	36	53	33	31
	4	$1s_{1/2}$	6795	7229	6873	7193	7141	7165	
		$2s_{1/2}$	792	883	835	857	899	843	
		$2p_{1/2}$	677	781	722	754	792	738	
		$2p_{3/2}$	665	768	710	741	779	725	
		$3s_{1/2}$	121	150	145	139	160	135	
		$3p_{1/2}$	90	117	113	105	127	102	
		$3p_{3/2}$	88	115	111	105	126	101	
		$3d_{3/2}$	40	61	56	52	70	49	
	5	$1s_{1/2}$	6814	7248	6898	7213	7162	7186	
		$2s_{1/2}$	811	902	857	877	920	864	
		$2p_{1/2}$	696	800	745	774	813	759	
		$2p_{3/2}$	684	787	733	761	800	747	
		$3s_{1/2}$	139	168	165	159	180	155	
		$3p_{1/2}$	107	135	133	126	147	122	
		$3d_{3/2}$	56	79	79	71	88	68	
	6	$1s_{1/2}$	6836	7271	6926	7237	7187	7211	
		$2s_{1/2}$	833	924	883	901	945	889	
		$2p_{1/2}$	718	822	771	798	838	784	
		$2p_{3/2}$	707	810	759	785	825	772	
		$3s_{1/2}$	159	189	187	181	202	178	
		$3p_{1/2}$	127	155	155	148	168	144	
		$3p_{3/2}$	126	154	153	146	166	143	
		$3d_{3/2}$	75	99	100	92	109	91	
	7	$1s_{1/2}$	6862	7297	6958	7263	7216	7240	
		$2s_{1/2}$	859	950	912	928	973	917	
		$2p_{1/2}$	744	848	800	824	866	812	
		$2p_{3/2}$	732	835	789	812	853	800	
		$3s_{1/2}$	182	212	212	205	225	202	
		$3p_{1/2}$	150	178	179	172	191	169	
		$3d_{3/2}$	96	123	124	116	131	114	151
	8	$1s_{1/2}$	6892	7326	6994	7294	7248	7272	
		$2s_{1/2}$	888	978	945	958	1004	948	
		$2p_{1/2}$	773	877	834	855	897	844	
		$2p_{3/2}$	761	864	822	842	884	831	
		$3s_{1/2}$	207	237	239	231	250	229	
		$3p_{1/2}$	174	203	206	198	216	195	
		$3p_{3/2}$	173	202	204	196	214	194	235
	9	$1s_{1/2}$	6926	7360	7034	7329	7284	7308	
		$2s_{1/2}$	920	1011	981	992	1038	983	
		$2p_{1/2}$	805	910	871	888	932	879	
		$2p_{3/2}$	794	897	859	876	919	866	
		$3s_{1/2}$	234	265	268	260	276	258	
		$3p_{1/2}$	201	231	235	226	242	224	
		$3p_{3/2}$	200	229	233	224	240	223	262
	10	$1s_{1/2}$	6963	7398	7079	7367	7324	7348	
		$2s_{1/2}$	956	1047	1022	1029	1077	1022	
		$2p_{1/2}$	842	946	912	927	971	918	
		$2p_{3/2}$	830	934	900	914	957	905	
		$3s_{1/2}$	264	295	300	291	304	289	
		$3p_{1/2}$	230	261	266	256	269	255	
		$3p_{3/2}$	228	259	264	255	267	253	290

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APPENDIX A: ORTHOGONALITY OF THE WAVE FUNCTIONS

In all our modified models (TFM, FAM, and TFDM), the differential equations, which yield the binding energies as eigenvalues, may be written symbolically

$$H\Psi_i=\epsilon_i\Psi_i\,, \tag{A1}$$

where

$$H=H^0+eV_i\,.$$

H^0 is an Hermitian operator and V_i is the self-potential corresponding to the state i. The operator H itself is, of course, not Hermitian, nor even linear, and its eigenfunctions are not necessarily orthogonal. The deviation from orthogonality may be estimated as follows: Let Ψ_1 and Ψ_2 be two eigenfunctions having the same angular momentum (otherwise orthogonality is automatically satisfied), but belonging to different principal quantum numbers n_1 and n_2, and let $n_1<n_2$. Now

$$(\Psi_1,H^0\Psi_2)=(\Psi_1,H\Psi_2)-(\Psi_1,eV_2\Psi_2)=\epsilon_2(\Psi_1,\Psi_2)-(\Psi_1,eV_2\Psi_2)\,, \tag{A2}$$

and similarly

$$(\Psi_1,H^0\Psi_2)=\epsilon_1(\Psi_1,\Psi_2)-(\Psi_1,eV_1\Psi_2)\,. \tag{A2$'$}$$

Hence,

$$\delta=|(\Psi_1,\Psi_2)|=|(\Psi_1,e(V_1-V_2)\Psi_2)|/|\epsilon_1-\epsilon_2|\,. \tag{A3}$$

Since $n_1<n_2$, it follows that $\epsilon_1<\epsilon_2<0$, and we may assume that $|V_1(r)-V_2(r)|$ is a monotonic decreasing function (i.e., in any sphere around the nucleus there is more charge due to state 1 than due to state 2). Therefore, we have

$$|(\Psi_1,(V_1-V_2)\Psi_2)|<|V_1(0)-V_2(0)|(|\Psi_1|,|\Psi_2|)\,. \tag{A4}$$

By Schwartz's inequality we have $(|\Psi_1|,|\Psi_2|)<1$, and therefore

$$\delta<e|V_1(0)-V_2(0)|/|\epsilon_1-\epsilon_2|\,. \tag{A5}$$

An upper bound for V_i is assumed to be the quantity $Ze/(a_0n_i^2)$; therefore, a very pessimistic estimate may be

$$\delta<(Ze^2/a_0|\epsilon_1-\epsilon_2|)(1/n_1^2-1/n_2^2)\,. \tag{A6}$$

Since $(\epsilon_1-\epsilon_2)$ is proportional to Z^2, δ is proportional to $1/Z$. In fact, the upper bound for δ is too high and may be easily reduced by a factor of 2 because of the different number of modes of the two functions. A calculation shows that δ is even much smaller. For example: For the $1s_{1/2}$ and $2s_{1/2}$ levels of an Al II ion, $\delta\approx0.18$ according to Eq. (A5), whereas an exact calculation yields $\delta=0.017$. Similar calculations show that in fact δ is always less than $1/2Z$.

APPENDIX B: REARRANGEMENT ENERGY

The eigenvalues calculated in the present paper are assumed to be the exact binding energies of the electrons according to the model. This is true only if the charge distribution of all electrons except the one considered is the same before and after removing the electron. This is not rigorously fulfilled and the charge distribution of the remaining $N-1$ electrons does certainly change. We may estimate the effect of rearrangement on the binding energies for the modified models.

Let ϵ_i^0 and Ψ_i^0 be the eigenvalue and the eigenfunction of the ith electron with the potential V_e+Ze/r; let ϵ_i be the eigenvalue of this electron with the potential $V_e+Ze/r-V_i^0$ (where V_i^0 is the potential associated with the function Ψ_i^0). We may write

$$\epsilon_i=\epsilon_i^0+\Delta\epsilon_i+\delta\epsilon_i\,, \tag{B1}$$

where $\Delta\epsilon_i=(\Psi_i^0,V_i^0\Psi_i^0)$ is the first-order correction to the eigenvalue according to perturbation theory. $\Delta\epsilon_i$ is obviously the correction to the binding energy, assuming that the wave functions of *all* electrons (including the ith) remain unchanged, whereas $\delta\epsilon_i$ is due to change of the wave function of the ith electron itself. Now, it is found by calculation that $\delta\epsilon_i$ is, except for the K shell, of the order of a few tenths of an eV. $\delta\epsilon_i$ may be regarded as the change of energy due to 'rearrangement' of the ith electron charge. The rearrangement energy of electrons belonging to the same shell may be assumed to be of the order of $\delta\epsilon_i$, whereas the rearrangement effects of the other electrons are probably much less: The inner electrons suffer but a very slight change in the electrostatic field exerted on them, and their rearrangement effects may be neglected; the outer electrons would also suffer a change which is on the average much less than the change of the field in the shell of the ith electron. Therefore, the order of magnitude of the rearrangement energy may be estimated by $0.2N$ eV, and is negligible in most cases.