Density-functional formulas for atomic electronic energy components in terms of moments of the electron density

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Reasoning from known identities arising from scaling considerations, formulas in terms of only the moments of the electron density, $M_k=\langle r^k\rho\rangle$, are developed for all energy components in the density-functional theory of the ground states of atoms. In particular, employing Hartree-Fock data for the first 54 atoms and many of their ions, it is demonstrated that formulas of the form $T_S=\Sigma_{k=1}^4 A_k(M_{-2/k})^k$ and $E_x=\Sigma_{k=1}^4 C_k(M_{-1/k})^k$ fit the neutral atoms He through Xe with standard deviations of 0.26% and 0.70%, respectively.
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I. INTRODUCTION

The fact that the classical moments of an electron density determine the electron density [1] and that the electron density of an electronic ground state determines all ground-state properties [2] implies that it is possible in principle to construct a theory for determining all properties in terms of moments. A previous paper [3] explored how to do this for the energy components E_c and T_c for atoms. In the present paper we study T_s and E_x and put forward and test for atoms universal expansions of these in terms of moments. We also propose how to express the total energy functional as a universal function of moments.

II. THEORY

The total energy of an atom can be written as

$$E[\rho]=T_S[\rho]+V_{\rm ne}[\rho]+J[\rho]+E_x[\rho]+E_c[\rho], \tag{1}$$

where $T_S[\rho]$, $V_{\rm ne}[\rho]$, $J[\rho]$, $E_x[\rho]$, and $E_c[\rho]$ are the noninteracting kinetic energy, the nuclear-electron interaction energy, the classical Coulomb electron-electron repulsion energy, the exchange energy, and the correlation energy, respectively. For an atom with atomic number Z,

$$V_{\rm ne}[\rho]=Z\langle r^{-1}\rangle=ZM_{-1}. \tag{2}$$

Here M_{-1} is one of the classical moments

$$M_k=\int r^k\rho(\mathbf{r})d\mathbf{r}, \tag{3}$$

where the nucleus has been taken as the origin. [For molecules, one might contemplate using moments about only one center (as, for example, in CH_4), or about two or more centers (as for diatomics).] What we shall seek are expressions for T_S, E_x, and E_c in terms of these M_k, and J as well. Note that Z itself also is expressible in terms of moments: For neutral atoms, for example, $Z=M_0=N$.

Governing equations, arising essentially from scaling arguments, are, for T_S [4],

$$T_S[\rho]=-\tfrac{1}{2}\int \rho(\mathbf{r})\mathbf{r}\cdot\nabla\frac{\delta T_S[\rho]}{\delta\rho(\mathbf{r})}d\mathbf{r}. \tag{4}$$

For E_x [5],

$$E_x[\rho]=-\int \rho(\mathbf{r})\mathbf{r}\cdot\nabla\frac{\delta E_x[\rho]}{\delta\rho(\mathbf{r})}d\mathbf{r}. \tag{5}$$

For E_c [6],

$$\lambda\frac{\partial E_c^\lambda[\rho]}{\partial\lambda}=E_c^\lambda[\rho]+\int \rho(\mathbf{r})\mathbf{r}\cdot\nabla\frac{\delta E_c^\lambda[\rho]}{\partial\rho(\mathbf{r})}d\mathbf{r}. \tag{6}$$

Here λ is the familiar coupling constant in the adiabatic connection; $\lambda=1$ gives the atom of interest: $E_c^1=E_c$.

Now it can be verified by direct substitution in Eqs. (4), (5), and (6), respectively, that particular solutions are [7]

$$T_S=(M_{-2/k})^k \quad \text{for any } k, \tag{7}$$

$$E_x=(M_{-1/k})^k \quad \text{for any } k, \tag{8}$$

and

$$E_c=\lambda^{lk+1}(M_l)^k \quad \text{for any } k \text{ and } l. \tag{9}$$

Other solutions of Eqs. (4)–(6) are possible, but we note how many there are of the forms of Eqs. (7)–(9) and expect good accuracy if we expand in terms of these. Accordingly for $\lambda=1$ we try expansions of the forms

$$T_S=\sum_k A_k(M_{-2/k})^k, \tag{10}$$

$$E_x=\sum_k C_k(M_{-1/k})^k, \tag{11}$$

and

$$E_c=\sum_{kl} D_{kl}(M_l)^k. \tag{12}$$

The constants A_k, C_k, D_{kl} remain to be determined. Values of k and l need not be integral.

Finally, J satisfies the same equation as E_x, Eq. (5), and so it should possess an expansion of the form of Eq. (11), namely (with $k=2$, $B_k \approx 0.27$ the major term)

$$J = \sum_k B_k (M_{-1/k})^k. \tag{13}$$

The inference then is that the total energy of Eq. (1) is expressible completely in terms of the moments of the electron density, for neutral atoms,

$$E = \sum_k A_k (M_{-2/k})^k + \sum_k B_k (M_{-1/k})^k + \sum_k C_k (M_{-1/k})^k + \sum_{kl} D_{kl} (M_l)^k - M_0 M_{-1}, \tag{14}$$

where the different sums correspond to Eqs. (10)–(13) and the last term is the nuclear-electron attraction. For an ion, M_0 would be replaced by M_0 plus an appropriate integer.

Equation (14) is enticing but at this stage is purely formal. It may be tested for accuracy, universality, and workability. To the extent that it is accurate, it would be a remarkable representation of the exact universal density functional for atoms.

We mention in passing that Dehesa, Galvez, and Porres [8] derived lower bounds to the kinetic energy;

$$T_S \geqslant \tilde{C}_k \langle r^{-(2/k)} \rangle^k \quad \text{for any } k, \tag{15}$$

and upper bounds to the exchange energies,

$$E_x \geqslant \tilde{B}_k \langle r^{-(1/k)} \rangle^k \quad \text{for any } k, \tag{16}$$

in the plane-wave approximation, where $\tilde{B}_k$ and $\tilde{C}_k$ depend only on the number of electrons, i.e., constant for a given system. It is interesting to ask whether expressions similar to Eqs. (10)–(13) can take lower or upper bounds.

III. TESTS

Here we confine the tests to tests of Eqs. (10) and (11). As ''accurate'' densities we take restricted Hartree-Fock densities [9], as ''accurate'' T_S values we take the negative Hartree-Fock energies, and as ''accurate'' E_x we take the Hartree-Fock exchanges. These are approximations which are known to be good ones. We do least-squares fits of percentage differences between calculated and accurate values. Using data for neutral atoms from $Z=2$ to 54, we somewhat arbitrarily choose to determine the following four-parameter fits for T_S and E_x, in accord with Eqs. (10) and (11):

TABLE I. Accurate and fitted kinetic energy values (in a.u.) for the first 54 neutral atoms. Fitted parameters: $A_1 = 1.798\,83 \times 10^{-1}$, $A_2 = 6.224\,11 \times 10^{-2}$, $A_3 = -8.888\,19 \times 10^{-4}$, $A_4 = 7.296\,27 \times 10^{-6}$. Standard deviation: 0.26%.

Z	Accurate	Fitted	Δ	Error%	Z	Accurate	Fitted	Δ	Error%
2	2.8617	2.8492	−0.0125	−0.436	29	1638.964	1644.122	5.1584	0.315
3	7.4327	7.4076	−0.0251	−0.338	30	1777.848	1783.663	5.8147	0.327
4	14.573	14.6042	0.0311	0.214	31	1923.261	1928.926	5.6649	0.295
5	24.5291	24.5507	0.0216	0.088	32	2075.36	2080.888	5.528	0.266
6	37.6886	37.6903	0.0017	0.005	33	2234.239	2239.651	5.4118	0.242
7	54.4009	54.4107	0.0098	0.018	34	2399.868	2405.077	5.209	0.217
8	74.8094	74.9819	0.1726	0.231	35	2572.441	2577.554	5.1127	0.199
9	99.4094	99.9232	0.5138	0.517	36	2752.055	2757.201	5.1458	0.187
10	128.5471	129.6839	1.1368	0.884	37	2938.357	2941.312	2.9541	0.101
11	161.8589	162.6058	0.7469	0.461	38	3131.546	3132.207	0.6612	0.021
12	199.6146	200.1024	0.4877	0.244	39	3331.684	3330.859	−0.825	−0.025
13	241.8767	241.9091	0.0324	0.013	40	3538.995	3537.035	−1.9604	−0.055
14	288.8544	288.5007	−0.3537	−0.122	41	3753.598	3751.891	−1.7064	−0.045
15	340.7188	340.0626	−0.6562	−0.193	42	3975.55	3973.452	−2.0983	−0.053
16	397.5048	396.6219	−0.8829	−0.222	43	4204.789	4200.972	−3.8174	−0.091
17	459.4821	458.52	−0.9621	−0.209	44	4441.54	4439.206	−2.3338	−0.053
18	526.8175	525.9534	−0.8641	−0.164	45	4685.882	4684.007	−1.8752	−0.040
19	599.1648	597.0401	−2.1247	−0.355	46	4937.921	4938.819	0.8974	0.018
20	676.7582	673.3736	−3.3846	−0.500	47	5197.698	5198.123	0.4249	0.008
21	759.7357	756.0062	−3.7295	−0.491	48	5465.133	5465.118	−0.0152	0.000
22	848.4061	844.6151	−3.7909	−0.447	49	5740.169	5739.028	−1.1414	−0.020
23	942.8844	939.2629	−3.6215	−0.384	50	6022.932	6020.935	−1.9969	−0.033
24	1043.356	1041.368	−1.9886	−0.191	51	6313.486	6310.917	−2.5691	−0.041
25	1149.866	1147.372	−2.4941	−0.217	52	6611.785	6608.794	−2.9905	−0.045
26	1262.444	1260.868	−1.5754	−0.125	53	6917.981	6914.999	−2.9816	−0.043
27	1381.414	1381.107	−0.3077	−0.022	54	7232.139	7229.654	−2.4845	−0.034
28	1506.871	1508.192	1.3214	0.088					

TABLE II. Accurate and fitted exchange energy values (in a.u.) for the first 54 neutral atoms. Fitted parameters: $C_1=-2.734\,83\times10^{-1}$, $C_2=-1.818\,14\times10^{-2}$, $C_3=3.613\,45\times10^{-4}$, $C_4=-3.148\,48\times10^{-6}$. Standard deviation: 0.70%.

Z	Accurate	Fitted	Δ	Error%	Z	Accurate	Fitted	Δ	Error%
2	−1.026	−1.026	0	0.002	29	−65.793	−66.0423	−0.2493	0.379
3	−1.781	−1.7892	−0.0082	0.461	30	−69.64	−69.7871	−0.1471	0.211
4	−2.667	−2.7146	−0.0476	1.784	31	−73.517	−73.5272	−0.0102	0.014
5	−3.744	−3.7882	−0.0442	1.18	32	−77.444	−77.3566	0.0874	−0.113
6	−5.045	−5.0429	0.0021	−0.041	33	−81.432	−81.2697	0.1623	−0.199
7	−6.596	−6.4869	0.1091	−1.655	34	−85.493	−85.2434	0.2496	−0.292
8	−8.174	−8.1009	0.0731	−0.895	35	−89.635	−89.306	0.329	−0.367
9	−10	−9.9187	0.0813	−0.813	36	−93.852	−93.4581	0.3939	−0.42
10	−12.11	−11.9472	0.1628	−1.344	37	−97.895	−97.4126	0.4824	−0.493
11	−14.02	−13.8322	0.1878	−1.339	38	−101.953	−101.448	0.5046	−0.495
12	−15.99	−15.8498	0.1402	−0.877	39	−106.185	−105.677	0.5084	−0.479
13	−18.07	−17.9446	0.1254	−0.694	40	−110.542	−110.024	0.5184	−0.469
14	−20.28	−20.1692	0.1108	−0.546	41	−115.122	−114.613	0.5091	−0.442
15	−22.64	−22.5198	0.1202	−0.531	42	−119.69	−119.189	0.5006	−0.418
16	−25	−24.9745	0.0255	−0.102	43	−124.169	−123.688	0.4807	−0.387
17	−27.15	−27.5556	−0.0456	0.166	44	−129.123	−128.609	0.5141	−0.398
18	−30.19	−30.2627	−0.0727	0.241	45	−133.989	−133.488	0.5014	−0.374
19	−32.677	−32.8147	−0.1377	0.421	46	−139.142	−138.669	0.4727	−0.34
20	−35.212	−35.4606	−0.2486	0.706	47	−144.04	−143.601	0.4391	−0.305
21	−38.031	−38.3581	−0.3271	0.86	48	−148.916	−148.617	0.2988	−0.201
22	−40.993	−41.3902	−0.3972	0.969	49	−153.826	−153.663	0.1633	−0.106
23	−44.089	−44.5409	−0.4519	1.025	50	−158.78	−158.829	−0.0487	0.031
24	−47.489	−47.988	−0.499	1.051	51	−163.766	−164.112	−0.3459	0.211
25	−50.686	−51.1984	−0.5124	1.011	52	−168.825	−169.493	−0.668	0.396
26	−54.19	−54.677	−0.487	0.899	53	−173.924	−175.004	−1.0797	0.621
27	−57.835	−58.2781	−0.4431	0.766	54	−179.092	−180.649	−1.557	0.869
28	−61.624	−61.9957	−0.3717	0.603					

TABLE III. Accurate and predicted kinetic energies (in a.u.) for the first positive ions of the first 54 atoms.

Z	Accurate	Predicted	Δ	Error%	Z	Accurate	Predicted	Δ	Error%
3	7.2364	7.1199	−0.1165	−1.61	30	1777.568	1781.199	3.6317	0.204
4	14.2774	14.0849	−0.1925	−1.348	31	1923.06	1927.017	3.9575	0.206
5	24.2376	24.057	−0.1805	−0.745	32	2075.087	2078.597	3.5106	0.169
6	37.2922	36.9155	−0.3768	−1.01	33	2233.888	2236.954	3.0657	0.137
7	53.888	53.2845	−0.6035	−1.12	34	2399.559	2402.216	2.6572	0.111
8	74.3726	73.5722	−0.8004	−1.076	35	2572.045	2574.263	2.2175	0.086
9	98.8317	98.0439	−0.7878	−0.797	36	2751.568	2753.454	1.8867	0.069
10	127.8178	127.2582	−0.5596	−0.438	37	2938.22	2939.911	1.6915	0.058
11	161.677	161.6815	0.0045	0.003	38	3131.374	3130.54	−0.8336	−0.027
12	199.3718	198.9123	−0.4595	−0.23	39	3331.473	3327.981	−3.4923	−0.105
13	241.6748	240.8662	−0.8085	−0.335	40	3538.809	3535.017	−3.7923	−0.107
14	288.5731	287.1545	−1.4186	−0.492	41	3753.39	3749.729	−3.6604	−0.098
15	340.3498	338.3831	−1.9667	−0.578	42	3975.334	3971.036	−4.2975	−0.108
16	397.1732	394.7438	−2.4294	−0.612	43	4204.594	4198.343	−6.2518	−0.149
17	459.0487	456.2655	−2.7832	−0.606	44	4441.322	4436.33	−4.9916	−0.112
18	526.2745	523.2894	−2.9851	−0.567	45	4685.664	4680.885	−4.7796	−0.102
19	599.0176	596.0155	−3.0021	−0.501	46	4937.676	4933.528	−4.1478	−0.084
20	676.57	672.1405	−4.4295	−0.655	47	5197.482	5194.469	−3.0128	−0.058
21	759.5391	754.6693	−4.8698	−0.641	48	5464.879	5461.027	−3.8522	−0.07
22	848.2035	843.1706	−5.0329	−0.593	49	5739.978	5735.385	−4.5924	−0.08
23	942.6708	938.8123	−3.8585	−0.409	50	6022.679	6016.692	−5.987	−0.099
24	1043.139	1039.764	−3.375	−0.324	51	6313.166	6306.038	−7.1273	−0.113
25	1149.649	1145.611	−4.0381	−0.351	52	6611.504	6603.545	−7.9593	−0.12
26	1262.213	1258.975	−3.2378	−0.257	53	6917.628	6909.065	−8.5627	−0.124
27	1381.129	1380.615	−0.5137	−0.037	54	7231.709	7222.988	−8.7206	−0.121
28	1506.591	1507.736	1.1446	0.076	55	7553.811	7545.443	−8.3677	−0.111
29	1638.728	1641.956	3.2282	0.197					

TABLE IV. Accurate and predicted exchange energies (in a.u.) for the first positive ions of the first 54 atoms.

Z	Accurate	Predicted	Δ	Error%	Z	Accurate	Predicted	Δ	Error%
3	−1.652	−1.635	0.017	−1.032	30	−69.511	−69.3793	0.1317	−0.189
4	−2.507	−2.5022	0.0048	−0.191	31	−73.344	−73.1589	0.1851	−0.252
5	−3.492	−3.536	−0.044	1.261	32	−77.242	−76.9505	0.2915	−0.377
6	−4.712	−4.7284	−0.0164	0.348	33	−81.201	−80.826	0.375	−0.462
7	−6.124	−6.1063	0.0177	−0.289	34	−85.227	−84.7857	0.4413	−0.518
8	−7.739	−7.6785	0.0605	−0.781	35	−89.332	−88.8116	0.5204	−0.583
9	−9.566	−9.4275	0.1385	−1.448	36	−93.109	−92.9258	0.1832	−0.197
10	−11.617	−11.3846	0.2324	−2.000	37	−97.812	−97.1294	0.6826	−0.698
11	−13.902	−13.5567	0.3453	−2.484	38	−101.86	−101.134	0.7261	−0.713
12	−15.863	−15.5335	0.3295	−2.077	39	−105.93	−105.207	0.7232	−0.683
13	−17.893	−17.6314	0.2616	−1.462	40	−110.25	−109.666	0.584	−0.53
14	−20.045	−19.8104	0.2346	−1.170	41	−114.67	−114.24	0.4302	−0.375
15	−22.307	−22.116	0.191	−0.856	42	−119.42	−118.786	0.6339	−0.531
16	−24.687	−24.5473	0.1397	−0.566	43	−124.06	−123.254	0.8064	−0.65
17	−27.075	−27.0857	−0.0107	0.040	44	−128.53	−128.147	0.383	−0.298
18	−29.82	−29.7501	0.0699	−0.235	45	−133.65	−132.994	0.6562	−0.491
19	−32.294	−32.5403	−0.2463	0.763	46	−138.58	−137.954	0.6258	−0.452
20	−35.108	−35.1598	−0.0518	0.148	47	−143.95	−143.037	0.9132	−0.634
21	−37.673	−38.0461	−0.3731	0.99	48	−148.78	−148.002	0.7782	−0.523
22	−40.621	−41.0666	−0.4456	1.097	49	−153.66	−153.056	0.6044	−0.393
23	−43.703	−44.3779	−0.6749	1.544	50	−158.59	−158.152	0.4378	−0.276
24	−46.917	−47.6544	−0.7374	1.572	51	−163.56	−163.363	0.1969	−0.12
25	−50.572	−50.8448	−0.2728	0.539	52	−168.58	−168.692	−0.112	0.066
26	−53.752	−54.3127	−0.5607	1.043	53	−173.66	−174.125	−0.4652	0.268
27	−57.379	−58.1012	−0.7222	1.259	54	−178.81	−179.688	−0.8783	0.491
28	−61.149	−61.8194	−0.6704	1.096	55	−184.02	−185.387	−1.3671	0.743
29	−65.063	−65.6606	−0.5976	0.919					

TABLE V. Accurate and predicted kinetic energies (in a.u.) for the first negative ions of the first 54 atoms.

Z	Accurate	Predicted	Δ	Error%	Z	Accurate	Predicted	Δ	Error%
1	0.4879	0.5035	0.0156	3.187	29	1638.964	1645.136	6.1713	0.377
3	7.4282	7.5101	0.0818	1.102	31	1923.26	1929.91	6.6491	0.346
5	24.5192	24.8141	0.2949	1.203	32	2075.395	2082.387	6.9918	0.337
6	37.7088	38.1689	0.4600	1.220	33	2234.223	2241.285	7.0621	0.316
7	54.322	55.0409	0.7189	1.323	34	2399.905	2407.141	7.2358	0.302
8	74.7897	75.921	1.1313	1.513	35	2572.536	2580.065	7.529	0.293
9	99.4595	101.2416	1.7821	1.792	37	2938.355	2941.94	3.5851	0.122
11	161.8552	162.9941	1.139	0.704	39	3331.683	3331.613	−0.0699	−0.002
13	241.8782	242.491	0.6128	0.253	40	3538.994	3539.098	0.1035	0.003
14	288.8897	289.3899	0.5002	0.173	41	3753.579	3753.106	−0.4723	−0.013
15	340.6989	341.0853	0.3864	0.113	42	3975.526	3974.772	−0.7548	−0.019
16	397.5385	397.9597	0.4213	0.106	43	4204.765	4203.875	−0.8901	−0.021
17	459.5769	460.2052	0.6283	0.137	44	4441.528	4440.89	−0.6383	−0.014
19	599.1619	597.4543	−1.7076	−0.285	45	4685.876	4685.889	0.0128	0.000
21	759.6887	757.2551	−2.4336	−0.320	46	4937.892	4939.005	1.1132	0.023
22	848.3725	846.0763	−2.2962	−0.271	47	5197.7	5200.443	2.7425	0.053
23	942.8631	940.9228	−1.9402	−0.206	49	5740.176	5741.674	1.498	0.026
24	1043.337	1042.031	−1.3065	−0.125	50	6022.973	6024.352	1.3795	0.023
25	1149.729	1149.209	−0.5198	−0.045	51	6313.481	6314.67	1.1884	0.019
26	1262.367	1262.974	0.6064	0.048	52	6611.828	6613.243	1.415	0.021
27	1381.352	1383.424	2.0723	0.150	53	6918.077	6920.179	2.1029	0.030
28	1506.821	1510.73	3.9085	0.259					

TABLE VI. Accurate and predicted exchange energies (in a.u.) for the first negative ions of the first 54 atoms.

Z	Accurate	Predicted	Δ	Error%	Z	Accurate	Predicted	Δ	Error%
1	−0.3955	−0.416	−0.0205	5.183	29	−65.846	−66.2906	−0.4446	0.675
3	−1.827	−1.8781	−0.0511	2.797	31	−73.595	−73.7775	−0.1825	0.248
5	−3.843	−3.9571	−0.1141	2.968	32	−77.564	−77.6753	−0.1113	0.143
6	−5.15	−5.2781	−0.1281	2.488	33	−81.587	−81.6051	−0.0181	0.022
7	−6.648	−6.755	−0.107	1.61	34	−86.2	−85.6242	0.5758	−0.668
8	−8.352	−8.4327	−0.0807	0.966	35	−89.852	−89.7315	0.1205	−0.134
9	−10.274	−10.3173	−0.0433	0.422	37	−97.925	−97.5915	0.3335	−0.341
11	−14.062	−14.0052	0.0568	−0.404	39	−106.32	−105.886	0.4337	−0.408
13	−18.15	−18.1693	−0.0193	0.106	40	−110.71	−110.403	0.3074	−0.278
14	−20.373	−20.4535	−0.0805	0.395	41	−115.17	−114.89	0.2797	−0.243
15	−22.711	−22.8264	−0.1154	0.508	42	−119.74	−119.485	0.2549	−0.213
16	−25.168	−25.3271	−0.1591	0.632	43	−124.38	−124.165	0.2151	−0.173
17	−27.749	−27.9537	−0.2047	0.738	44	−129.17	−128.96	0.2105	−0.163
19	−32.715	−32.9848	−0.2698	0.825	45	−134	−133.868	0.1319	−0.098
21	−38.203	−38.681	−0.478	1.251	46	−139.01	−138.895	0.1151	−0.083
22	−41.173	−41.7369	−0.5639	1.37	47	−144.09	−144.048	0.0417	−0.029
23	−44.283	−44.9074	−0.6244	1.41	49	−153.91	−154.181	−0.2706	0.176
24	−47.535	−48.1998	−0.6648	1.399	50	−158.89	−159.446	−0.5559	0.35
25	−50.917	−51.5789	−0.6619	1.3	51	−163.92	−164.782	−0.8618	0.526
26	−54.436	−55.081	−0.645	1.185	52	−168.99	−170.248	−1.2576	0.744
27	−58.095	−58.6991	−0.6041	1.04	53	−174.13	−175.846	−1.7161	0.986
28	−61.899	−62.4336	−0.5346	0.864					

TABLE VII. Accurate and predicted kinetic energies (in a.u.) for the Be isoelectronic ion series from Be to Ca^{+16}.

Z	Accurate	Predicted	Δ	Error%
4	14.5728	14.6051	0.0323	0.222
5	24.2376	24.0584	−0.1792	−0.739
6	36.4087	35.8784	−0.5303	−1.457
7	51.0826	50.0633	−1.0192	−1.995
8	68.2576	66.6138	−1.6438	−2.408
9	87.9354	85.5295	−2.4059	−2.736
10	110.111	106.814	−3.297	−2.994
11	134.7889	130.4641	−4.3248	−3.209
12	161.9721	156.4915	−5.4806	−3.384
13	191.6461	184.8639	−6.7822	−3.539
14	223.8251	215.6135	−8.2117	−3.669
15	258.5049	248.7296	−9.7753	−3.781
16	295.6797	284.2002	−11.4794	−3.882
17	335.3583	322.0491	−13.3092	−3.969
18	377.5395	362.2652	−15.2742	−4.046
19	422.2128	404.8338	−17.3789	−4.116
20	469.3899	449.7826	−19.6073	−4.177

TABLE VIII. Accurate and exchange energies (in a.u.) for the Be isoelectronic ion series from Be to Ca^{+16}.

Z	Accurate	Predicted	Δ	Error%
4	−2.667	−2.7146	−0.0476	1.783
5	−3.492	−3.536	−0.044	1.261
6	−4.314	−4.3543	−0.0403	0.934
7	−5.135	−5.1713	−0.0363	0.708
8	−5.956	−5.9878	−0.0318	0.534
9	−6.776	−6.8041	−0.0281	0.414
10	−7.596	−7.6201	−0.0241	0.317
11	−8.415	−8.4361	−0.0211	0.25
12	−9.235	−9.2527	−0.0177	0.192
13	−10.054	−10.0679	−0.0139	0.138
14	−10.874	−10.8835	−0.0095	0.087
15	−11.693	−11.6992	−0.0062	0.053
16	−12.513	−12.5147	−0.0018	0.014
17	−13.332	−13.3304	0.0016	−0.012
18	−14.152	−14.1462	0.0058	−0.041
19	−14.971	−14.9616	0.0094	−0.063
20	−15.79	−15.7772	0.0128	−0.081

TABLE IX. Accurate and predicted kinetic energies (in a.u.) for the Ne^{+n} positive ion series $n=0-7$.

n	Accurate	Predicted	Δ	Error%
0	128.5512	129.6891	1.1379	0.885
1	127.8215	127.2637	−0.5578	−0.436
2	126.3763	124.2399	−2.1364	−1.691
3	124.1083	120.6761	−3.4322	−2.765
4	120.5491	116.4369	−4.1122	−3.411
5	115.9152	111.7783	−4.1368	−3.569
6	110.1162	106.7741	−3.3421	−3.035
7	102.6362	99.023	−3.6132	−3.52

TABLE X. Accurate and predicted exchange energies (in a.u.) for the Ne^{+n} positive ion series $n=0-7$.

n	Accurate	Predicted	Δ	Error%
0	−12.1080	−11.9613	0.1467	−1.212
1	−11.6170	−11.3987	0.2183	−1.879
2	−10.9940	−10.7612	0.2328	−2.117
3	−10.2650	−10.0614	0.2036	−1.983
4	−9.4460	−9.2879	0.1581	−1.673
5	−8.5520	−8.4753	0.0767	−0.896
6	−7.5960	−7.6343	−0.0383	0.504
7	−6.8430	−6.7743	0.0687	−1.004

$$T_S=A_1M_{-2}+A_2(M_{-1})^2+A_3(M_{-2/3})^3+A_4(M_{-1/2})^4, \tag{17}$$

$$E_x=C_1M_{-1}+C_2(M_{-1/2})^2+C_3(M_{-1/3})^3+C_4(M_{-1/4})^4. \tag{18}$$

Least-squares-fitted results are given in Tables I and II.

Predictability is tested in Tables III–X, in which the same formulas (and same constants) are used to predict T_S and E_x for all of the monopositive and mononegative ions, for the Be isoelectronic series Be, B^+, C^{2+}, etc., and for the Ne ions Ne^+, Ne^{2+}, etc. For $N=Z=86$, Eq. (17) predicts a kinetic energy 4.5% too large, and Eq. (18) predicts an exchange energy 27% too negative.

IV. DISCUSSION

The formulas for T_S and E_x of Eqs. (17) and (18) are seen to be remarkably accurate and highly transferable. Note that the formulas we have obtained are ''universal'' in the sense that they are expressed in terms of the density only. The atomic number and electron number: do not enter the formulas. The good fit for positive ions is particularly encouraging. Because the present work is exploratory, we do not compare accuracy here with accuracy of other functionals.

Putting everything in terms of moments, as in Eq. (14), with integer k values, amounts to a complete discretization of the density-functional theory. Noting, for example, that $\langle \rho\,\delta M_k/\delta\rho\rangle = M_k$ and $\langle \rho\,\delta M_k/\delta\rho\rangle^l = lM_k^l$, we see that the moments and their powers give corresponding potentials with nice analytical properties, which lends hope that the same parameters A_k, B_k, C_k, and D_{kl} may serve to represent well both E and $\delta E/\delta\rho$. (The last is a severe test, however.) Derivation of some or all the constants from first principles should be attempted. Representation by truncated versions of Eq. (14) may or may not have appropriate behavior at nuclear cusps and at long range, and they may or may not satisfy other conditions known from works of Levy *et al.* [5] to be satisfied by exact functionals. Extension to molecules will be possible; see the remark after Eq. (3) above.

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