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Atomic Correlation Energy from the Electron Density at the Nucleus[†]

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Ground-state atomic correlation energies, and their kinetic energy and potential energy components, are shown to be well-represented by empirical formulas of the form $CN\rho(0)Z^{-\gamma}$, where C and γ are constants that are largely invariant within various sets of atoms and positive ions, Z is the atomic number, N is the number of electrons, and $\rho(0)$ is the electron density at the nucleus. Results are given for neutral atoms, singly charged positive ions, and many isoelectronic series—315 atomic species in all.

I. Introduction

Given the present availability of numerical values for atomic Hartree−Fock energies (E_{HF}) and atomic total electronic energies (E), it is timely to study directly the atomic correlation energies

$$E_C = E_{HF} - E \tag{1}$$

Effectively treating E_C directly would provide relief from calculating first E_{HF} and then E by conventional methods.

We speculate that given the accurate Hartree−Fock wavefunction, there may be a way to produce a good, physically sound, semiempirical method to obtain E_C directly, using no more information than in the Hartree−Fock wavefunction, or even just the Hartree−Fock electron density. What we shall show here is that in fact one can go far by employing just the Hartree−Fock electron density at the nucleus, $\rho(0)$. We were prompted to try this because of our success with this within density functional theory.[1]

So, we set out to study the validity, for many atomic species, of scaling formulas of the form

$$E_C = CN\rho(0)/Z^{\gamma} \tag{2}$$

where Z is the atomic number, N is the number of electrons, γ is a constant, and so is C. For a particular series of species, we take the test of validity of this formula to be whether a particular choice of C and γ well-represent known data.

II. Results from E_C Fittings

To test formulas of the form of eq 2, the data needed are Z, N, and accurate values of ground-state $\rho(0)$ and E_C for each species. These are taken from the literature and are listed in the first columns of Tables 1−4.[2−4] In the fits reported, simple least-squares was used for determination of C, and sometimes also γ, not on eq 2 but on the equivalent

$$\ln E_C = \ln C + \ln N + \ln \rho(0) - \gamma \ln Z \tag{3}$$

TABLE 1: Test of Eq 4 for Neutral Atoms and Singly Charged Ions[a]

	E_C	$\rho(0)$	C_2		E_C	$\rho(0)$	C_2
He	0.0420	3.6	0.037	Na$^+$	0.389	833.2	0.028
Li$^+$	0.0435	13.7	0.030	Na	0.396	833.8	0.026
Li	0.045	13.8	0.020	Mg$^+$	0.400	1092.9	0.025
Be$^+$	0.047	35.1	0.018	Mg	0.438	1093.7	0.025
Be	0.094	35.4	0.027	Al$^+$	0.452	1403.8	0.025
B$^+$	0.111	72.6	0.028	Al	0.470	1402.9	0.024
B	0.125	71.9	0.025	Si$^+$	0.486	1766.8	0.024
C$^+$	0.139	128.5	0.026	Si	0.505	1765.7	0.023
C	0.156	127.5	0.024	P$^+$	0.522	2187.8	0.023
N$^+$	0.167	207.3	0.024	P	0.540	2186.4	0.023
N	0.199	206.1	0.025	S$^+$	0.556	2671.1	0.023
O$^+$	0.194	313.3	0.023	S	0.605	2669.5	0.023
O	0.258	311.7	0.026	Cl$^+$	0.622	3221.0	0.023
F$^+$	0.261	450.2	0.025	Cl	0.666	3219.2	0.023
F	0.325	448.3	0.028	Ar$^+$	0.683	3841.8	0.023
Ne$^+$	0.325	622.2	0.027	Ar	0.722	3839.8	0.023
Ne	0.390	619.9	0.029	K$^+$	0.739	4537.9	0.023

[a] C_2 values are calculated from accurate E_C and $\rho(0)$ values. See the text.

We first try the two forms of eq 2 that stood out in the density functional study,[1]

$$E_C = C_2 N\rho(0)Z^{-8/3} \tag{4}$$

and

$$E_C = D_2 N\rho(0)Z^{-3} \tag{5}$$

Results are displayed in Tables 1−3.

Table 1 exhibits the results of employing eqs 4 and 5 for neutral atoms and their single-charged cation from $N = 2$ to 18, He to K$^+$. We see that C_2 values are almost constant through the series, converging at higher Z to 0.023, the same limiting value as that for the density-functional T_c.[1] Table 2 shows the results for the $N = 10$ isoelectronic series from Ne to Ni^{18+}. Here, though C_2 is slowing converging, D_2 values are more uniform, implying that eq 5 is the better fit for the $N = 10$ series. Neither C_2 and D_2 works so well with the Be isoelectronic series, but there is a fine fit if we use constant B_2 in the formula

$$E_C = B_2 NZ^{-7/3}\rho(0) \tag{6}$$

This is demonstrated in Table 3 (atomic units throughout).

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TABLE 2: Test of Eqs 4 and 5 for Ne ($N = 10$) Isoelectronic Series Ions[a]

	Z	E_C	$\rho(0)$	C_2	D_2
Ne	10	0.3905	619.9	0.029	0.063
Na^+	11	0.3889	833.2	0.028	0.062
Mg^{2+}	12	0.3896	1091.2	0.027	0.062
Al^{3+}	13	0.3911	1398.3	0.026	0.061
Si^{4+}	14	0.3928	1758.6	0.025	0.061
P^{5+}	15	0.3946	2176.6	0.025	0.061
S^{6+}	16	0.3962	2656.4	0.024	0.061
Cl^{7+}	17	0.3978	3202.5	0.024	0.061
Ar^{8+}	18	0.3992	3819.0	0.023	0.061
K^{9+}	19	0.4005	4510.3	0.023	0.061
Ca^{10+}	20	0.4017	5280.6	0.022	0.061
Sc^{11+}	21	0.4028	6134.4	0.022	0.061
Ti^{12+}	22	0.4038	7075.8	0.022	0.061
V^{13+}	23	0.4048	8109.2	0.021	0.061
Cr^{14+}	24	0.4056	9238.9	0.021	0.061
Mn^{15+}	25	0.4064	10469.1	0.021	0.061
Fe^{16+}	26	0.4072	11804.2	0.020	0.061
Co^{17+}	27	0.4079	13248.4	0.020	0.061
Ni^{18+}	28	0.4085	14806.1	0.020	0.061

[a] C_2 and D_2 values are calculated from accurate E_C and $\rho(0)$ values. See the text.

TABLE 3: Test of Eqs 4 and 5 for Be ($N = 4$) Isoelectronic Series[a]

	Z	$\rho(0)$	E_C	C_2	B_2
Be	4	35.4	0.094	0.027	0.017
B^+	5	72.6	0.111	0.028	0.016
C^{2+}	6	129.8	0.126	0.029	0.016
N^{3+}	7	211.3	0.141	0.030	0.016
O^{4+}	8	321.3	0.154	0.031	0.015
F^{5+}	9	464.2	0.167	0.032	0.015
Ne^{6+}	10	644.1	0.180	0.032	0.015
Na^{7+}	11	865.6	0.192	0.033	0.015
Mg^{8+}	12	1132.8	0.205	0.034	0.015
Al^{9+}	13	1450	0.217	0.035	0.015
Si^{10+}	14	1821.5	0.230	0.036	0.015
P^{11+}	15	2251.7	0.242	0.037	0.015
S^{12+}	16	2744.8	0.254	0.038	0.015
Cl^{13+}	17	3305.1	0.266	0.038	0.015
Ar^{14+}	18	3937	0.278	0.039	0.015
K^{15+}	19	4644.7	0.290	0.040	0.015
Ca^{16+}	20	5432.4	0.302	0.041	0.015
Sc^{17+}	21	6304.6	0.314	0.042	0.015
Ti^{18+}	22	7265.6	0.326	0.043	0.015
V^{19+}	23	8319.5	0.338	0.043	0.015
Cr^{20+}	24	9470.7	0.350	0.044	0.015
Mn^{21+}	25	10722.71	0.361	0.045	0.015
Fe^{22+}	26	12081.35	0.373	0.046	0.015
Co^{23+}	27	13550.19	0.385	0.047	0.016
Ni^{24+}	28	15133.51	0.397	0.047	0.016

[a] C_2 and B_2 values are calculated from accurate E_C and $\rho(0)$ values. See the text.

To approach a higher accuracy, we relax the restriction that γ is $^8/_3$ or 3 and choose γ to be separately determined for each isoelectronic series. We simply do a least-square fit of eq 3 for each series, thereby determining "best" values of C and γ for a particular series. Results are summarized in Table 4. The accuracy is phenomenal, with the average absolute error in E_C on the order of 1 kcal/mol, as shown in the table. "Chemical accuracy" has been achieved!

TABLE 4: Least-Square Fits of Eq 3 for Isoelectronic Series from He ($N = 2$) to Ar ($N = 18$)[a]

N	C	γ	R^2	no. of data points	av absolute error in au	av absolute error in kcal/mol
2	0.0467	3.0796	0.9999	19	0.0008	0.40
3	0.0302	3.0381	1.0000	26	0.0003	0.17
4	0.0166	2.3632	0.9996	25	0.0054	3.36
5	0.0209	2.5655	0.9998	24	0.0036	2.24
6	0.0292	2.7720	1.0000	23	0.0015	0.92
7	0.0446	2.9838	1.0000	22	0.0007	0.46
8	0.0518	2.9907	1.0000	21	0.0003	0.17
9	0.0591	3.0079	1.0000	20	0.0005	0.33
10	0.0664	3.0285	1.0000	19	0.0012	0.74
11	0.0567	2.9938	1.0000	18	0.0004	0.24
12	0.0380	2.8285	1.0000	17	0.0008	0.48
13	0.0321	2.7743	1.0000	16	0.0016	0.98
14	0.0296	2.7545	1.0000	15	0.0015	0.96
15	0.0287	2.7525	1.0000	14	0.0013	0.79
16	0.0275	2.7289	1.0000	13	0.0014	0.85
17	0.0270	2.7177	1.0000	12	0.0009	0.59
18	0.0263	2.7087	1.0000	11	0.0004	0.28
average					0.0013	0.82

[a] For each series, accurate values of $\rho(0)$ are employed to determine best C and γ values by least-squares.

These results show that the total correlation energy E_C takes a different power-decaying form for different isoelectronic series. For $N = 2$, 3, 7−11, the optimal power-decaying γ value is approximately 3, whereas for $N = 6$, 12−18, it is close to $^8/_3$. For the series of $N = 4$ and 5, different γ values hold. Formulas of the form of eq 2 indeed work very well, but with γ and C best taken to be different for different isoelectronic series. Figure 1 depicts the overall situation.

If we put all 100 data points for $N = 7-11$ series together in one fit, the optimal γ value is 2.9624 with correlation coefficient $R^2 = 0.9916$. For $N = 6$, 12−18 series, a single fit of all 121 data points gives $\gamma = 2.7314$ with $R^2 = 0.9982$. For $N = 2$ and 3 series (45 data points), we obtain $\gamma = 3.1263$ and $R^2 = 0.9937$. For all 315 points together, $\gamma = 2.7373$ and $C = 0.02708$ with $R^2 = 0.9435$,

$$E_C/N = 0.027\rho(0)Z^{-2.74} \tag{7}$$

Equation 7 constitutes a refinement of a very old rule of quantum chemistry, that the correlation energy is about 1 eV per electron pair. Another work of this general kind, in which the correlation energy is related to the electrostatic potential at the nucleus, is due to Alonso et al.[5] Also see our own early work.[6]

III. Fittings Involving T_C and V_C

The findings above show that correlation energies $E_C(N,Z)$ of ground-state lighter atoms and ions can be nicely predicted from the electron density at the nucleus, $\rho(0)$. The formula is

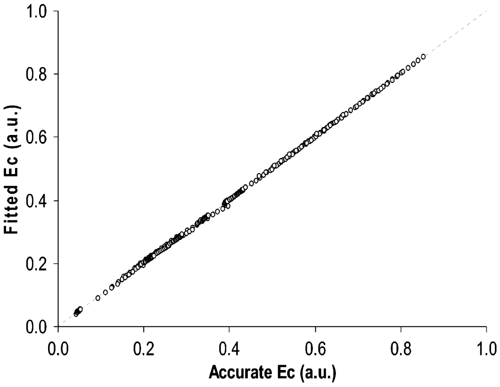

Figure 1. Computed correlation energies for atoms and ions (a total of 315 species). See the text and Table 4.

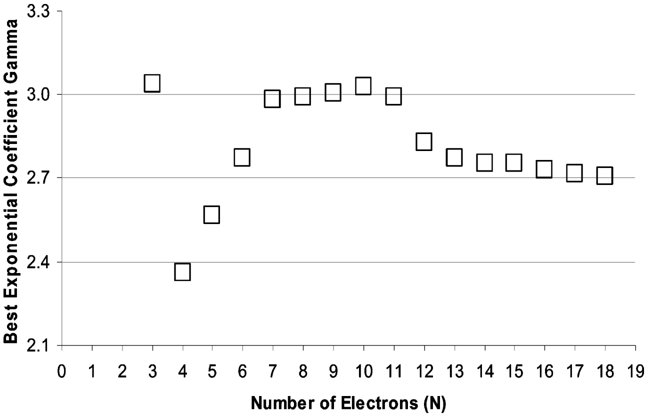

Figure 2. The fitted power-decaying coefficient for each of the isoelectronic series from $N = 2$ to $N = 18$. See the text and Table 4.

eq 2. In Table 4 are given C and γ values for 17 isoelectronic series. We note that γ is an irregular function of N, as shown in Figure 2.

We now explore the consequence of the virial theorem, which may or may not provide a deeper understanding of eq 2, as applied to the Hartree−Fock situation. We should emphasize that E_C in Hartree−Fock theory differs from E_C in density-functional theory as commonly defined. In Hartree−Fock theory we have

$$E_C = -T_C = {}^1\!/_2 V_C = T_C + V_C \tag{8}$$

where T_C, V_C, and E_C are defined in accordance with the tradition that an energy of correlation is the exact energy minus the Hartree−Fock energy. T_C is positive; V_C and E_C are both negative.

To decide how to model T_C and V_C separately, we adapt a primitive argument from ref 1. Consider the "cusp density",

$$\rho_M(\mathrm{r}) = \rho(0)\exp(-2Zr) \tag{9}$$

and compute the integrals

$$\left\langle \frac{\rho_M(r)}{r^k} \right\rangle = 4\pi\rho(0)\int e^{-2Z} r^{2-k}\,\mathrm{d}r = \frac{4\pi\rho(0)}{(2Z)^{3-k}} = C_k\rho(0)Z^{k-3} \tag{10}$$

In particular,

$$\left\langle \frac{\rho_M}{r} \right\rangle \propto Z^{-2}, \left\langle \frac{\rho_M}{r^2} \right\rangle \propto Z^{-1} \tag{11}$$

so that in eq 2, $\gamma = 1$ acts like a potential energy and $\gamma = 2$ like a kinetic energy. These exhibit homogeneous coordinate scalings of degree −1 and −2, respectively. The corresponding $\gamma = 1.74$ for neutral atoms (where $N = Z$) of eq 7 above is revealed as a reasonable compromise between kinetic and potential energies. And something we can try is fitting eq 2 separately for

$$T_C(N,Z) = C_T N\rho(0)Z^{-1} = -E_C \tag{12}$$

and

$${}^1\!/_2 V_C(N,Z) = C_V N\rho(0)Z^{-2} = -E_C \tag{13}$$

Again as before, we use known E_C data to determine empirical values of C_T and C_V.

TABLE 5: Fits for Neutral Atoms from He to Ar Employing Eqs 12 and 13[a]

Z	$\rho(0)$	PotFit	KinFit	AvgFit	MixFit	accurate E_C
2	3.6	0.010	0.050	0.030	0.040	0.040
3	13.8	0.020	0.088	0.054	0.063	0.045
4	35.4	0.038	0.128	0.083	0.095	0.094
5	71.9	0.062	0.166	0.114	0.128	0.125
6	127.5	0.091	0.204	0.148	0.163	0.156
7	206.1	0.127	0.243	0.185	0.199	0.199
8	311.7	0.168	0.281	0.224	0.238	0.258
9	448.3	0.214	0.319	0.267	0.279	0.325
10	619.9	0.267	0.358	0.312	0.322	0.390
11	833.8	0.326	0.398	0.362	0.368	0.396
12	1093.7	0.392	0.438	0.415	0.417	0.438
13	1402.9	0.464	0.479	0.472	0.468	0.470
14	1765.7	0.542	0.520	0.531	0.522	0.505
15	2186.4	0.627	0.561	0.594	0.577	0.540
16	2669.5	0.717	0.602	0.660	0.635	0.605
17	3219.2	0.814	0.643	0.728	0.695	0.666
18	3839.8	0.917	0.684	0.801	0.757	0.722
av abs error		0.0788	0.0230	0.0509	0.0212	

[a] Fits defined as follows: KinFit, $E_C = 0.0043N\rho(0)/Z$; PotFit, $E_C = 0.0577N\rho(0)/Z^2$; AvgFit, $E_C = (\text{KinFit} + \text{PotFit})/2 = 0.0288N\rho(0)/Z^2 + 0.0022N\rho(0)/Z$; MixFit, $E_C = 0.0369N\rho(0)/Z^2 + 0.0015N\rho(0)/Z$.

TABLE 6: Fits for Be Isoelectronic Series from Be to Ni^{24+} Employing Eqs 12 and 13[a]

atom	$\rho(0)$	PotFit	KinFit	AvgFit	MixFit	accurate E_C
Be	35.4	0.050	0.258	0.154	0.098	0.094
B^+	72.6	0.065	0.271	0.168	0.113	0.111
C^{2+}	129.8	0.081	0.281	0.181	0.127	0.126
N^{3+}	211.3	0.097	0.288	0.192	0.141	0.141
O^{4+}	321.3	0.112	0.293	0.203	0.154	0.154
F^{5+}	464.2	0.128	0.297	0.213	0.167	0.167
Ne^{6+}	644.1	0.144	0.301	0.223	0.180	0.180
Na^{7+}	865.6	0.160	0.304	0.232	0.192	0.192
Mg^{8+}	1132.8	0.176	0.306	0.241	0.205	0.205
Al^{9+}	1450.0	0.192	0.308	0.250	0.217	0.217
Si^{10+}	1821.5	0.208	0.310	0.259	0.230	0.230
P^{11+}	2251.7	0.224	0.312	0.268	0.242	0.242
S^{12+}	2744.8	0.240	0.313	0.277	0.254	0.254
Cl^{13+}	3305.1	0.256	0.314	0.285	0.267	0.266
Ar^{14+}	3937.0	0.272	0.315	0.294	0.279	0.278
K^{15+}	4644.7	0.288	0.316	0.302	0.291	0.290
Ca^{16+}	5432.4	0.304	0.317	0.311	0.303	0.302
Sc^{17+}	6304.6	0.320	0.318	0.319	0.316	0.314
Ti^{18+}	7265.6	0.336	0.319	0.328	0.328	0.326
V^{19+}	8319.5	0.352	0.319	0.336	0.340	0.338
Cr^{20+}	9470.7	0.368	0.320	0.344	0.352	0.350
Mn^{21+}	10722.7	0.384	0.321	0.352	0.364	0.361
Fe^{22+}	12081.4	0.400	0.321	0.361	0.376	0.373
Co^{23+}	13550.2	0.416	0.322	0.369	0.389	0.385
Ni^{24+}	15133.5	0.432	0.322	0.377	0.401	0.397
av abs error		0.0117	0.0328	0.0223	0.0011	

[a] Fits defined as follows: KinFit, $E_C = 0.0056N\rho(0)/Z^2$; PotFit, $E_C = 0.1167N\rho(0)/Z^3$; AvgFit, $E_C = (\text{KinFit} + \text{PotFit})/2 = 0.0584N\rho(0)/Z^3 + 0.0028N\rho(0)/Z^2$; MixFit, $E_C = 0.0277N\rho(0)/Z^3 + 0.0042N\rho(0)/Z^2$.

Shown in Tables 5 and 6 are the fits of eqs 12 and 13 for neutral atoms from He to Ar and the Be isoelectronic series. Also tabulated are the results from an average of the two formulas and from the best linear combination of them. The average absolute errors for the four fits are also shown. It is seen that for the neutral species in Table 5, eq 12 performs better than eq 13, whereas for the Be isoelectronic series in Table 6 it is eq 13 that outperforms. Combination fits give significantly better results than one-term fits.

These results are comparably satisfactory to those in the last section, showing that scaling models of correlation effects can be extended to separately model the kinetic and potential energy effects.

IV. Discussion

We have verified that once $\rho(0)$ is known for an atom, the Hartree−Fock correlation energy and its kinetic and potential components can be estimated from formulas of the simple scaling form: constant times $\rho(0)$ time N times Z to a negative power, or from one such form representing the kinetic energy component plus a second representing the potential energy component. Specific formulas are given in the text. Accuracy reaches toward 1 kcal/mol.

More work is needed. In the first place, the seeming utility of the "cusp density", $\rho(0)\exp(-2Zr) = \rho_M(r)$, in rationalizing our results, calls for addressing the problem of finding why this works so well. How do we generate from fundamental theory the fact that correlation energy is well-expressed as a constant times the electron density at the nucleus, with the constant the number of electrons divided by a power of the atomic number? Helpful for future work in this area will be generating, by conventional quantum-mechanical methods or experiments, actual values of electron densities at nuclei. Molecules should be investigated, as well as excited states of atoms and molecules.

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