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COMPARISON BETWEEN TWO DIFFERENT APPROACHES TOWARD ATOMIC RADII

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Abstract: A numerical test for a new recently proposed scale of atomic radii is presented. Comparison of results between a hybrid-density functional calculation atomic scale and data resulting from Dirac-Breit shows a quite satisfactory agreement. Multivariate regression analysis is employed in order to look for the best possible fitting polynomials and to surmount some limitations of the simple linear relationships.

INTRODUCTION

The availability to both experimental and theoretical researchers of atomic data is important since those data may be of use either as point of reference or as basis for future work. The Hartree-Fock results for energies and coupling constants, atomic properties, and parameters and integrals of interest are tabulated for the ground states of the neutral atoms of the Periodic System in compilations that constitutes the final extension of some previously published data **[1]**. Atomic radius can be considered among the most relevant atomic parameters, and it may be defined in several ways. In atomic calculations it represents the radius corresponding to the maximum charge density in the outermost orbital.

However, different authors have defined atomic radii in different ways and each alternative possess their relative merits, although such arbitrariness degree has given raise to a rather large number of atomic radius scales. In a recent paper, Suresh and Koga have presented a consistent approach toward atomic radii (R_A) based on hybrid-density functional calculations on methyl group substituted elemental hydrides of the form $H_3C\text{-}EH_n$ (E is any main block or d block transition element and n is 0, 1, 2, 3, or 4 depending on the position of E in the Periodic Table) **[2]**. R_A is given as the C-E bond distance minus half of the C-C bond distance of ethane and it shows good linear correlations with the experimental covalent radii, Slater's empirical set of atomic radii, and experimental carbon-based atomic radii particularly for the main block elements. Later on, improved correlations were presented among R_A and covalent radius ($R_{covalent}$), Clementi, Raimondi, and Reinhardt atomic radii (R_{CRR}), Slater's radii (R_{Slater}), and Alcock's radii (R_{Alcock}) for elements belonging to the main block and d block transition group **[3]**.

The quite satisfactory agreement among those atomic radii scales has led us to analyze to correlation between R_A and atomic radius data resulting from quantum-mechanical calculations performed via Dirac-Breit equation **[1]** (R_{DB}). This first-principles approach is more accurate than that given by Clementi *et al* from minimal-basis-set SCF wave functions for ground-state atoms **[4]**, so that the present approach makes up a more demanding test for R_A data.

CALCULATION METHOD

Simple regression involving but a single independent variable restricts regression analysis considerably. Many correlations need not be linear. In fact, a quadratic regression may result in a better description of the relationship than a simple model. Non-linear models may be fitted to data sets by the inclusion of functions of the independent variable in a linear regression model **[5]**. Construction of linear regression models containing non-linear terms is most often prompted when the data is clearly not well fitted by a linear model, but where regularity in the data suggests that some other model will fit. In general, one should test single descriptor regression for quadratic dependence and, if warranted, for higher order polynomial relationships or other functional dependence **[6]**.

In this work we present results for linear, quadratic, and cubic correlations between R_A and atomic radii from Fraga *et al*'s book **[1]**. The data were taken from Refs. 1 and 2 and the corresponding values are given in Tables 1 and 2 for main block elements and *d* block transition elements. Calculations were performed using the standard MATHEMATICA® software **[7]**.

RESULTS AND DISCUSSION

Linear, quadratic and cubic polynomial fitting equations between R_A versus R_{DB} were determined for elements cited in Tables 1 and 2 resorting to standard multilinear regression techniques **[8]**. Multilinear regression analysis was performed up to the third order since for higher order results do not change appreciably. Statistical parameters for polynomial fitting equations are given in Table 3. Finally, in Table 4 some representative results are given for illustrative purposes. Complete results can be requested to the corresponding author.

Analysis of results displayed in Table 3 allows us to see that in general the statistical parameters are quite satisfactory for different relationships. Calculations of R_A values on the basis of R_{DB} data are better for main block elements than for d block transition elements. The employment of second- and third-order does not show a significant improvement in final results with respect to linear fitting polynomials, although regression coefficients and standard errors of estimate for d block transition elements are somewhat better than those corresponding to linear formula. Predictions given in Table 4 for elements are quite satisfactory, since there is not any "pathological behavior", and deviations are in general, rather small.

In closing, we deem present approach to predict R_A values for main block elements and d block transition elements from accurate Dirac-Breit calculation scheme of atomic wavefunctions is quite satisfactory and it constitutes a rather simple and direct procedure.

These numerical features corroborates that the new calculation procedure of atomic radii on the basis of hybrid-density functional calculations is satisfactory and it adds to the set of accepted current proposals to obtain this atomic property.

Table 1. Atomic radii (in Å) for main block elements.

Atom	**R_A [2]**	**R_{BD} [1]**
Li	1.219	1.67
Be	0.911	1.11
B	0.793	0.83
C	0.766	0.65
N	0.699	0.52
O	0.658	0.46
F	0.633	0.41
Na	1.545	1.80
Mg	1.333	1.37
Al	1.199	1.43
Si	1.123	1.18
P	1.110	0.97
S	1.071	0.85
Cl	1.039	0.75
K	1.978	2.35
Ca	1.745	1.85
Zn	1.187	1.24
Ga	1.199	1.44
Ge	1.179	1.16
As	1.209	1.06
Se	1.201	0.96
Br	1.201	0.88
Rb	2.217	2.56
Sr	1.928	2.07
Cd	1.429	1.36
In	1.385	1.60
Sn	1.380	1.39
Sb	1.421	1.28
Te	1.400	1.18
I	1.397	1.08
Cs	2.442	2.84
Ba	2.149	2.31
Hg	1.465	1.43
Tl	1.531	1.70
Pb	1.434	1.48
Bi	1.496	1.38

Table 2. Atomic radii (in Å) for *d* block transition elements.

Atom	**R_A [2]**	**R_{BD} [1]**
Sc	1.337	1.77
Ti	1.274	1.58
V	1.236	1.52
Cr	1.128	1.45
Mn	1.180	1.39
Fe	1.091	1.34
Co	1.089	1.29
Ni	1.077	1.24
Cu	1.146	1.20
Y	1.482	1.89
Zr	1.377	1.84
Nb	1.353	1.69
Mo	1.240	1.65
Tc	1.287	1.61
Ru	1.212	1.57
Rh	1.229	1.45
Pd	1.240	1.42
Ag	1.362	1.39
La	1.653	2.27
Hf	1.364	1.80
Ta	1.346	1.67
W	1.256	1.64
Re	1.258	1.62
Os	1.222	1.60
Ir	1.227	1.48
Pt	1.227	1.46
Au	1.273	1.45

Table 3. Coefficients and statistical parameters for correlations equations R_A versus R_{DB} of main block elements and d block transition elements.

Correlation	**Coefficients**[1]				**R**[2]	**S**[3]
	a	**b**	**c**	**d**		
R_A vs R_{DB}	***d block transition elements***					
Linear	0.4998	0.4889			0.8941	0.0565
Quadratic	0.9462	-0.0557	0.1625		0.9007	0.0559
Cubic	0.7867	0.2379	-0.0138	0.0345	0.9008	0.0571
R_A vs R_{DB}	***main block elements***					
Linear	0.3354	0.7325			0.9442	0.1505
Quadratic	0.3100	0.7723	-0.0131		0.9443	0.1526
Cubic	-0.0136	1.6786	-0.6854	0.1447	0.9482	0.1494

[1] $R_A = bR_{DB} + c[R_{DB}]^2 + d[R_{DB}]^3 + a$

[2] Regression coefficient.

[3] Standard error of estimate.

Table 4. Some predicted radii for main block elements and d block transition elements derived from the multilinear regression equations.

Atom	**R_{DB}**[1]	**Deviation**	**Atom**	**R_{DB}**[2]	**Deviation**
Li	1.532	-0.313	***Ti***	1.264	0.010
Be	1.183	-0.272	***V***	1.237	-0.001
B	0.970	-0.177	***Cr***	1.207	-0.079
C	0.808	-0.042	***Mn***	1.183	-0.003
N	0.674	0.025	***Fe***	1.163	-0.072
O	0.608	0.050	***Co***	1.145	-0.056
F	0.549	0.084	***Ni***	1.127	-0.050
Na	1.611	-0.066	***Cu***	1.113	0.033
Mg	1.352	-0.019	***Y***	1.421	0.061
Al	1.388	-0.189	***Zr***	1.394	-0.017
Si	1.231	-0.108	***Nb***	1.316	0.037
P	1.082	0.028	***Mo***	1.297	-0.057
S	0.987	0.084	***Tc***	1.278	0.009
Cl	0.901	0.138	***Ru***	1.259	-0.047
K	2.004	-0.026	***Rh***	1.207	0.022
Ca	1.642	0.103	***Pd***	1.195	0.045
Zn	1.270	-0.083	***Ag***	1.183	0.179
Ga	1.394	-0.195	***La***	1.657	-0.004
Ge	1.217	-0.038	***Hf***	1.372	-0.008
As	1.148	0.061	***Ta***	1.306	0.040
Se	1.074	0.127	***W***	1.292	-0.036
Br	1.011	0.190	***Re***	1.282	-0.024
Rb	2.199	0.018	***Os***	1.273	-0.051
Sr	1.788	0.140	***Ir***	1.220	0.007
Cd	1.346	0.083	***Pt***	1.211	0.016
In	1.490	-0.105	***Au***	1.207	0.066
Sn	1.364	0.016	***Sc***	1.357	-0.020
Sb	1.295	0.126			
Te	1.231	0.169			
I	1.162	0.235			
Cs	2.520	-0.078			
Ba	1.970	0.179			
Hg	1.388	0.077			
Tl	1.550	-0.019			
Pb	1.418	0.016			
Bi	1.358	0.138			
Average absolute deviation	-	**0.106**	-	-	**0.039**

[1] Third-order regression equation.
[2] Second-order regression equation.

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