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A simple eigenvalue sum-density relationship for atoms

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In recent years several attempts have been made [1-3] to obtain an energy-eigenvalue sum relationship for atoms and molecules. Such studies are useful in providing a sound theoretical basis for the successful Walsh and Woodward-Hoffmann rules which are based on the eigenvalue sum, E^s, in place of the total energy E. Unfortunately a general quantitative energy-eigenvalue sum relationship is not as yet available.

The purpose of this letter is to approach the problem from the one electron density, $\rho(r)$, point of view. We shall be concerned with a given isoelectronic series of atoms. We propose that within such a series

$$E^s \approx C_1\langle\rho\rangle^{2/3} + C_2\langle\rho\rangle^{1/3} \tag{1}$$

where E^s denotes the eigenvalue-sum $\sum \nu_i\varepsilon_i$ and the average density expectation value is given by $\langle\rho\rangle = \int \rho^2 d\tau$. Hyman et al. [4] have obtained a reasonably tight lower bound on $E^{3/2}$ in terms of $\langle\rho\rangle$ which is given by

$$\frac{\langle\rho\rangle}{E^{3/2}} \leq 0.205. \tag{2}$$

These authors noted that the numerical value of the ratio $\langle\rho\rangle/E^{3/2}$ remains constant within an atomic N-electron series.

Based on the scaling arguments due to Szasz et al. [5] it has been shown [6] numerically that an excellent representation of the total electron-electron repulsion energy, V_{ee}, for atoms can be written as

$$V_{ee} = 0.3977 N^{4/3}\langle\rho\rangle^{1/3} \tag{3}$$

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using Eqs. (2)-(3), respectively, in the form

$$E = C_1\langle\rho\rangle^{2/3} \tag{4}$$

and

$$V_{ee} = C_2\langle\rho\rangle^{1/3} \tag{5}$$

in the Hartree-Fock (HF) identity

$$E^s = E + V_{ee} \tag{6}$$

leads to Eq. (1).

In Table 1 we have listed the values of the fitting parameters C_1 and C_2 corresponding to the He, Li, and Be isoelectronic series along with the regression coefficient 'r'. All the fits are found to have excellent 'r' values.

In Table 2 we have presented the values of $\langle\rho\rangle^{1/3}$ and E^s based on the analytic Hartree-Fock wave functions [7] and the values of E^s obtained from Eq. (1). These results show that Eq. (1) provides a good quantitative relationship for E^s in terms of $\langle\rho\rangle$. We also note that the quantity $2\langle\rho\rangle^{1/3}$ closely approximates the value of Z, the atomic number, and it is therefore tempting [8] to represent E^s and the total *HF* energy E in terms of a polynomial in $\langle\rho\rangle^{1/3}$. A polynomial fit

Table 1. Fitting parameters C_1 and C_2 in Eq. (1) for the He, Li, and Be isoelectronic series respectively

	Fitting parameters		
Series	$-C_1$	C_2	Regression coefficient
He	3.3975	1.1063	0.9999
Li	3.5160	1.6712	0.9999
Be	3.5972	2.3937	0.9999

Table 2. The values of $\langle\rho\rangle^{1/3}$ and $E^s(H.F.)$ based on the Hartree-Fock wave functions (Ref. 4 and Ref. 7) for some members of the He, Li, and Be series. E^s values obtained from Eq. (1) are given in the last column

Series	$\langle\rho\rangle^{1/3}$	E^s (*H.F.*)	E^s (Fitted)
He	0.9153	1.836	1.831
Li^+	1.4551	5.585	5.582
N^{5+}	3.6225	40.584	40.579
Li	1.4642	5.152	5.091
Be^+	2.0210	10.943	10.984
O^{5+}	4.2572	56.723	56.609
Be	2.0325	10.076	9.994
B^+	2.6060	18.119	18.192
O^{4+}	4.3353	57.366	57.232

Table 3. The fitting parameters given in Eq. (7) for He, Li, and Be-series corresponding to the total Hartree-Fock energy, E^{HF}, and the Hartree-Fock eigenvalue sum, E^{s}, respectively. The number(n) denotes $\times 10^{n}$. All values are in a.u.

Series		Fitting parameters					Average
		A	*B*	*C*	*D*	*E*	% error
He	E^{HF}	−3.406	−0.940 (−2)	−0.101 (−1)	−0.192 (−1)	0.261 (−1)	0.3 (−3)
	E^{S}	−3.406	1.152	−0.583 (−1)	0.999 (−2)	0.937 (−2)	0.6 (−3)
Li	E^{HF}	−3.590	0.243	−0.189	0.253	−0.161	0.8 (−3)
	E^{S}	−3.590	0.243	−0.189	0.253	−0.161	0.8 (−3)
Be	E^{HF}	−3.738	0.519	−0.381	0.696	−0.613	0.1 (−3)
	E^{S}	−3.729	3.111	−0.560	−0.921	0.705 (−1)	0.1 (−3)

of E^s (and E^{HF}) according to

$$E^s = A\langle\rho\rangle^{2/3} + B\langle\rho\rangle^{1/3} + C + D\langle\rho\rangle^{-1/3} + E\langle\rho\rangle^{-2/3} \tag{7}$$

is given in Table 3 for the He, Li and Be series respectively. Such polynomials can be used to obtain the estimates of E^s from the experimentally determined $\langle\rho\rangle$ values.

We wish to point out that Eq. (1) is only a semiempirical result in the sense that although its form can be arrived at in a purely theoretical manner, the actual constants C_1 and C_2 have been obtained using the available *HF* data. In the light of the existence of a unique energy density functional for the ground state of an *N*-electronic system [9] and Eq. (1), we conclude that the energy-eigenvalue sum relationship can be understood in terms of the single particle density.

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