

ON THE CONSISTENCY OF STATISTICAL RELATIONS
BETWEEN SINGLE AND DOUBLE IONISATION POTENTIALS AND ELECTRON
AFFINITIES OF NEUTRAL ATOMS AND MOLECULES

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ABSTRACT: A statistical relation between electron affinities and single ionization potentials given by Parr and Bartolotti is compared with a statistical relation between single and double ionization potentials of neutral atoms and molecules given by Tsai and Eland. It is shown that both relations are consistent, although the exponential form of the energy function proposed by Parr and Bartolotti would give an inconsistent relation. Further statistical relations and implications for the electronegativity equalization principle are discussed.

Experimental and theoretical interest in electron affinities of atoms and molecules/1/ and the still limited amount of data available/2,3/makes it desirable to have, in addition to computational methods, also qualitative, in fact even statistical rules for their estimation and correlation to other data. For instance, Lowe/4/ gave qualitative rules for relating molecular electron affinity values to the electron affinities of the corresponding atomic constituents. Also relations between electron affinities and ionization potentials are of interest in this respect. One step in that direction has been taken by Myers/5/ who considered

the electron affinities of atoms in relation to the ionization potential of their neighbour, in the table of elements, with atomic number larger by one and found smooth curvilinear relations for vertical groups in the periodic table.

A statistical relation between the electron affinity (EA) of a neutral atom to the ionization potential (IP) of the same atom has been established by Parr and Bartolotti^{6/}, namely

$$EA = (0.12 \pm 0.07) IP \quad (1)$$

It is easy to check that this can be generalized to hold not only for atoms, but also for molecules: Evaluating the EA/IP ratio for all neutral atoms and molecules for which IP- and EA-values are given in a recent reference book^{3/}, we find

$$EA = (0.13 \pm 0.09) IP \quad (2)$$

It is noteworthy that a similar statistical relation had been proposed to hold between the double-ionization potential (DIP) of a neutral atom or molecule and its single-ionization potential: Tsai and Eland^{7/} found, by evaluating average and standard deviation of the DIP/IP ratio for a large number of systems, that in the statistical sense

$$DIP = (2.8 \pm 0.1) IP \quad (3)$$

It is the purpose of the present note to discuss the consistency of equ. (2) with equ. (3).

The need for such a discussion becomes apparent if one considers the arguments of Parr and Bartolotti⁶ and tries to use them to derive equ. (3) in the same way they derived equ. (1). They proposed that the total energy of a system with N electrons, E(N), should be an exponentially decaying function of the number of electrons, i.e.

$$E(N) = A \exp [-\gamma (N-Z)] + B \quad (4)$$

where Z is the number of electrons when the system is neutral and A, B, γ are constants. For γ they obtained 2.15 ± 0.59 , and from the definitions $EA = E(Z) - E(Z+1)$ and $IP = E(Z-1) - E(Z)$ follows equ. (1). The same argument would yield

$$\begin{aligned} DIP &= E(Z-2) - E(Z) \\ &= (e^{2\gamma} - 1)(e^{\gamma} - 1)^{-1} IP \\ &= (9.58 \pm 5.06) IP \end{aligned} \quad (5)$$

which is in striking disagreement with equ.(3).

Let us point out immediately, therefore, that equs. (2) and (3) are indeed consistent in the sense that without knowledge of the specific properties of the systems involved one would infer one from the other.

To show this it is convenient to introduce in agreement with the concepts of statistical analysis /8/ the following

Definition: Two statistical relations

$$p_i(x_1, \dots, x_n) = 0 \quad ; i=1,2$$

constraining the values for a set of n physical observables x_j , are called consistent (in the sense of extrapolation) if there exists a (n-2)-th order collocation polynomial $f(j) \equiv F(x_1, \dots, x_{n-1}, j)$ such that

$$x_j = F(x_1, \dots, x_{n-1}, j) \quad ; j=1 \dots n-1$$

and that the two equations

$$p_i(x_1, \dots, x_{n-1}, F(x_1, \dots, x_{n-1}, n)) = 0 \quad ; i=1,2$$

are identical within the error limits.

We can then state the

Proposition: The two statistical relations

$$E(Z) - E(Z+1) - (0.13 \pm 0.09) [E(Z-1) - E(Z)] = 0$$

$$E(Z-2) - E(Z) - (2.8 \pm 0.1) [E(Z-1) - E(Z)] = 0$$

are consistent in the sense of the above definition.

Proof: Applying Sterling's formula for a second-order collocation polynomial to the total energy of a system with Z+K electrons we obtain

$$E(Z+K) = E(Z) + (K/2) [E(Z+1) - E(Z-1)] \\ + (K^2/2) [E(Z+1) - 2E(Z) + E(Z-1)]. \quad (6)$$

Inserting this with $K=-2$ into the second relation yields the first one within the error limits.

Remark 1: Equ.(6) yields an extrapolation formula:

$$\text{DIP} = 3 \text{ IP} - \text{EA} \quad (7)$$

Since in writing down the collocation polynomial we have ignored any specific properties of the systems, equ.(7) will not be a good approximation for individual systems, but should become valid for averages over many systems (as considered here).

Remark 2: Equ.(7) is related to Pariser's integral approximation /9/. Writing down the expression for the first DIP in a frozen-orbital Hartree-Fock approximation, assuming a closed-shell system with nondegenerate ground state, gives /7,10/

$$\text{DIP} \approx 2 \text{ IP} - V \quad (8)$$

where V is the Coulomb integral describing the repulsion of two electrons in the highest occupied orbital. Equ.(6) leads then to Pariser's approximation, $V \approx \text{IP} - \text{EA}$, which can thus be justified in the statistical average. The argument remains valid also if correlation is taken into account in a quasi-particle picture, by multiplying the integral with the corresponding renormalization factors /11/.

Corollary: Further relations can be obtained for multiple ionization: If Z is replaced by Z-1 in equ.(6) one obtains

$$\text{TIP} \approx 3 (\text{DIP} - \text{IP}) \quad (9)$$

where $\text{TIP} = E(Z-3) - E(Z)$ is the triple-ionization potential of the system. With equ.(1) follows $\text{TIP} \approx f^{(3)} \text{DIP}$ where $f^{(3)} = 3(1-\text{IP}/\text{DIP})$. Generalization of the argument to m-fold ionization yields the recursion formula

$$\text{IP}^{(m)} \approx f^{(m)} \text{IP}^{(m-1)} \quad (10)$$

where $\text{IP}^{(m)} = E(Z-m) - E(Z)$ and $f^{(m)} = 3(1-1/f^{(m-1)})$.

Equ.(10) will obviously progressively underestimate the $f^{(m)}$ with increasing m. For instance, employing equ.(1) would give $f^{(3)} = 1.93$ and $f^{(4)} = 1.44$, while the actual numbers obtained from the statistics of the data given in ref./3/are $f^{(3)} = 1.98 \pm 0.97$ and $f^{(4)} = 1.76 \pm 0.78$.

We return now to the consistency of the Parr-Bartolotti rule with the Tsai-Eland rule. The conclusion from the consistency of those relations and the disagreement of equ.(5) with the empirical Tsai-Eland rule is that is is the exponential form in equ.(4) for the energy function which does not permit a consistent prediction of multiple ionization potentials. The reason for proposing equ.(4) was/6/that it would satisfy the geometric mean principle for electronegativity equalization/2/(that the electronegativity of a molecule can be ap-

proximated by the geometric mean of the original atomic electronegativities). It should be mentioned, however, that the classical supposition¹³, that the energy is a second-order polynomial in the variable $(N-Z)$,

$$E(N) = a (N-Z) + b (N-Z)^2 \quad (12)$$

(with constants a, b), does not violate the consistency relation equ.(7) and would fulfill though not the geometric, but a corresponding arithmetic mean principle for electronegativity equalization.

Given the importance of electron affinities and ionization potentials (mostly treated only by standard computational schemes or accurate experimental measurements) on the one hand, the desirability of phenomenological rules for relations between them on the other hand, and regarding the consequences for the electronegativity equalization principle, we have here a perhaps interesting crosslink between areas which in part belong to the quantitative, -measuring or computing-, branch of physics and in part to an area of qualitative predictions, valuable for instance in chemical physics ¹⁴ /.

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