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Merit of ground-state electronegativities; a reply to "Comments on 'Introduction to the chemistry of fractionally charged atoms: Electronegativity' "

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The arguments presented in the Comment by Liebman and Huheey are shown to be incorrect. The operational equivalence of Mulliken ground-state electronegativities and Pauling electronegativities is demonstrated for neutral atoms. It is shown that ground-state electronegativities and valence-state electronegativities for both neutral atoms and ions are also operationally equivalent. A single electronegativity scale based on Mulliken ground-state electronegativities may therefore be used for neutral atoms, ions, and fractionally charged atoms, as originally implied in the paper by Lackner and Zweig.

I. SUMMARY OF CRITICISMS

In their Comment,[1] Liebman and Huheey claim that the electronegativity "values listed by Lackner and Zweig[2] are incorrect" because these values disagree with those established by Pauling. Liebman and Huheey argue further that the difference between Pauling's values for the electronegativity of the elements and the values given in Ref. 2 is a measure of the error in the latter values. They note that this "error" is 30—60 % of the change in electronegativity of a ground-state atom due to the addition of a charge of $\frac{1}{3}e$ to its nucleus. They imply that the electronegativities of the fractionally charged elements are in error by the same amount, rendering them essentially useless.

II. REPLY TO THE COMMENT

The claims and implications of the Comment are incorrect. They are based on an erroneous comparison of electronegativities derived from two different definitions. In addition, the Comment argues for the use of valence-state electronegativities without acknowledging that these arguments have already been presented in Ref. 2. The justification for these remarks now follows.

The Comment implies that there is one "traditional" (correct) value of electronegativity. In fact, there are several equally valid ways of defining electronegativity, each summarizing different but correlated chemical effects. Some definitions even assign several electronegativity values to the same element, giving one value for each valence state. All definitions try to approximate "the power of an atom in a molecule to attract electrons to itself."[3]

Pauling assigns a single electronegativity to each atom. Only the difference of electronegativities has chemical significance.[3] More precisely, the electronegativity difference between elements A and B, $\chi_P(A)-\chi_P(B)$, is defined in terms of the difference between the heteroatomic bond energy $E_{A\text{-}B}$ and the geometric mean of the homoatomic bond energies $E_{A\text{-}A}$ and $E_{B\text{-}B}$. In simple cases,

$$[\chi_P(A)-\chi_P(B)]^2 \equiv (E_{A\text{-}B}-\sqrt{E_{A\text{-}A}E_{B\text{-}B}})/30 , \qquad (1)$$

where the bond energies are measured in units of kcal/mole. The factor 30 is chosen for convenience to make the electronegativity difference between carbon and fluorine equal to 1.5. Pauling, also for convenience, fixes the absolute electronegativity scale by setting the electronegativity of fluorine equal to 4.0.

Mulliken, on the other hand, assigns multiple electronegativities to each element, one for each valence state.[4] The electronegativity χ_{VS} of a valence state is defined to be the average of its ionization potential and electron affinity:

$$\chi_{VS} \equiv \left[\frac{IP_{VS}+EA_{VS}}{2} \right] . \qquad (2)$$

Reference 2 adopted Mulliken's definition of electronegativity and extended it to atoms with fractionally charged nuclei. Ground-state electronegativities χ_{GS} were computed, and methods for determining electronegativities of other valence states were also indicated.

Mulliken ground-state electronegativities may be compared with Pauling electronegativities, if a conversion formula can be justified, but it is not possible to conclude from an apparent discrepancy that one or the other set of electronegativity values is "incorrect." However, this is done in the first paragraph of the Comment.

Table I of the Comment and its interpretation in the text are flawed in the same fashion. In addition, Liebman and Huheey average electronegativity values obtained from four different definitions and use this uninterpretable average in Table I as a standard against which the correctness of Mulliken ground-state electronegativities should be judged.[5]

The Comment is inappropriate because its authors are in effect comparing "apples with oranges" and complaining that they are not the same. They do not claim that there are any computational errors in the ground-state electronegativities, nor do they argue that any of the conclusions drawn in Ref. 2 from these electronegativity values are incorrect.

Liebman and Huheey also state that the electronegativities obtained in Ref. 2 are "incorrect" because they were given for ground states rather than for valence states. However, in Mulliken's definition each element has a multitude of electronegativity values, one of which corresponds to the ground state. In computing the transfer of charge from one atom to another in the formation of a molecule, the electronegativities that should be used are those associated with the valence states most closely representing the electron structure of the atoms in that molecule.

The authors of the Comment do not acknowledge that the computation of ground-state electronegativities serves as a convenient starting point for the computation of valence-state electronegativities.[6] They also do not acknowledge that Ref. 2 emphasized the importance of valence-state electronegativities and explained how they can be calculated from ground-state electronegativities. Liebman and Huheey appear not to realize that the example they use to demonstrate the importance of valence-state electronegativities is the example used in Ref. 2 to emphasize precisely this point. The Comment reads as follows.

> "The most obvious application of this idea [valence-state electronegativity] is that the appropriate electronegativity to use for carbon will be when it is sp^3, sp^2, or sp hybridized in alkanes, alkenes, and alkynes, *not* a pure p orbital. The appropriate promotion energies such as $2s^2 2p^2 \rightarrow 2(sp^3)^4$ must be included in the electronegativity calculation."

This is to be compared with the following passage from Ref. 2.

> "Although Mulliken's definition of [ground-state] electronegativity provides a good approximation to the power of an atom in a molecule to attract electrons, a better approximation takes the hybridization of the atomic electron orbitals into account.[6-10] [Reference numbers changed to those of this paper.] For example, the carbon atom in a molecule usually is not in its ground state (s^2p^2), but rather in an excited state, where the electron orbitals are linear combinations of the s and p states. There exist several such hybrids for carbon. (The carbon-hydrogen bond can involve three different hybrids: sp^3 as in ethane $H_3C\text{-}HC_3$; sp^2 as in ethylene $H_2C=CH_2$; sp^1 as in acetylene $HC\equiv HC$. The electron-attracting ability of an sp^n hybrid centered on carbon increases as the percentage of s character in the orbital increases.) In Eq. (6) [$\chi = 0.5(IP + EA)$], IP and EA should be taken to be the ionization potential and electron affinity of the hybrid [valence] state, rather than the ground state. In general, several electronegativities are assigned to an atom, one for each hybrid state. The energies of the hybrid states are calculated from experimental data (Refs. 6,8-10)."

The second example used in the Comment to illustrate the importance of valence states is also well known and dates back to Mulliken's original publication in 1934,[4] where HCl rather than HF is used. In this way Liebman and Huheey incorrectly make it appear as if the importance of valence states, which is fundamental to their Comment, is a new issue overlooked in Ref. 2.

Liebman and Huheey have also missed the essential conceptual point that electronegativities of atoms with fractionally charged nuclei can be found by interpolating along isolectronic sequences, while electronegativities of ordinary "partially charged atoms" cannot. In the first lines of their Comment, and implicitly in the text surrounding Eqs. (1) and (2), Liebman and Huheey state that the change in electronegativity resulting from a change in the electronic charge around an atom was correlated in Ref. 2 with the change of electronegativity resulting from a change in the nuclear charge of that atom. However, no such correlation was made, nor can it be made easily, as we now indicate.

The electronegativity is a function of the nuclear charge Z and the electron number N. Its functional dependence on Z for fixed N is usually smooth, while the variations with N for fixed Z are highly irregular due to changes in the electron shell structure. (See, for example, Fig. 3 of Ref. 2.) Therefore, correlating changes of the electronegativity in the Z and N directions is not simple and was not attempted.

Although Ref. 2 does not adopt Eqs. (1) and (2) of the Comment (originally given by Hinze and Jaffé[6]) because of difficulties in operationally defining nonintegral electron numbers q, it does show that the parameters a and b occurring in these equations are smooth functions of the nuclear charge Z, and computes $a(Z)$ and $b(Z)$ by interpolating along isoelectronic sequences of atoms and ions.[11]

III. THE MERIT OF GROUND-STATE ELECTRONEGATIVITIES

The thoughtful reader might, however, interject: "It may be true that Liebman and Huheey are wrong in calling Mulliken ground-state electronegativities 'incorrect.' They may also leave the reader with the incorrect impression that they have raised a new issue by pointing out the importance of valence-state electronegativities. The fact remains, though, that Lackner and Zweig only computed ground-state electronegativities, and ground-state electronegativities differ substantially from valence-state electronegativities. Moreover, if one converts ground-state electronegativities to the Pauling scale using a conventional formula,[12] then the values obtained differ substantially from Pauling's values. Lackner and Zweig's electronegativities are not 'incorrect,' but are they useful?" A reply to these remarks now follows.

The objective of Ref. 2 was to define a unified electronegativity scale for elements with integrally and fractionally charged nuclei. Contrary to the implications of the Comment, Mulliken ground-state electronegativities can be used for this purpose. Here it is crucial to note that any two definitions of electronegativity that are linearly related are operationally equivalent. If such a linear relation exists, electronegativity differences are equal up to an overall scale factor. Since it is only electronegativity differences that have chemical significance, the same conclusions will be drawn from either set of electronegativities. In fact, as Fig. 1 shows, the linear correlation between Mulliken ground-state electronegativities and Pauling electronegativities is remarkably strong, making the two scales for ordinary elements operationally equivalent. The linear relation is given by

$$\chi_{\mathrm{GS}}\ (\text{Pauling units}) = 4.08\chi_{\mathrm{GS}}\ (\text{MJ/mole}) + 0.10\ , \tag{3}$$

with a root-mean-square deviation of

$$\sigma \equiv \left[\frac{1}{M-2} \sum (\chi_{\mathrm{P}} - \chi_{\mathrm{GS}})^2 \right]^{1/2} = 0.24\ (\text{Pauling units})\ , \tag{4}$$

where M is the number of electronegativities that are correlated. χ_{GS} (Pauling units) is the Mulliken ground-state electronegativity converted to the Pauling scale, while χ_{GS} (MJ/mole) represents the same quantity in units of MJ/mole. The coefficients in Eq. (3) have been chosen to minimize σ.

The strong linear correlation is surprising since the chemical factors that determine Mulliken ground-state electronegativities and Pauling electronegativities are different. However, a strong linear correlation does not mean that the two definitions are physically equivalent. The only conclusion that can be drawn from such a correlation is that the sum of all those effects which distinguish one definition from the other can be represented by a linear function of either electronegativity.

The reason Liebman and Huheey obtain such large differences between Mulliken's ground-state electronegativities and Pauling's electronegativities is that they used a different conversion formula, one posited by Hinze and Jaffé[6] who correlated Pauling electronegativities with Mulliken valence-state electronegativities. Their relation is

$$\chi_{\mathrm{VS}}\ (\text{Pauling units}) = 3.48\chi_{\mathrm{VS}}\ (\text{MJ/mole}) - 0.21\ . \tag{5}$$

Liebman and Huheey did not point out that the differences they computed were not random but were linearly related to Pauling's electronegativity, as is evident from Fig. 1. This systematic linear deviation implies that the Pauling electronegativity scale and the Mulliken ground-

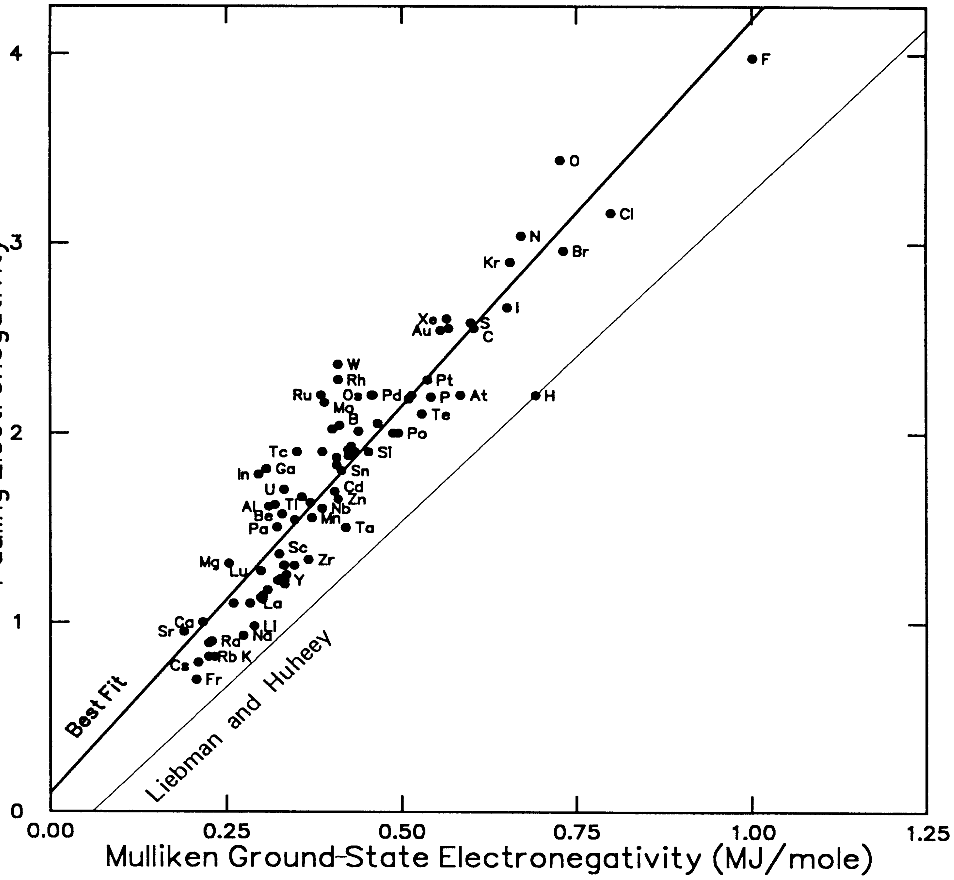

FIG. 1. Scatter plot demonstrating that Pauling electronegativities and Mulliken ground-state electronegativities are linearly correlated. The line labeled "Liebman and Huheey" represents the conversion formula the authors of the Comment used to create the large discrepancies presented in the first paragraph and Table I of their Comment.

state electronegativity scale are in fact operationally equivalent.

It is therefore appropriate to use Eq. (3) to correct the values given in the Comment representing deviations between ground-state electronegativities and Pauling electronegativities. Table I corrects the numbers given in the first paragraph of the Comment and Table II corrects Table I of the Comment. Table I of the Comment is further flawed by its use of an average of four differently defined electronegativities as the "standard of excellence." Since this average is uninterpretable,[5] Table III of this reply makes the analogous comparison with Pauling's electronegativities. The set of relatively small deviations now correctly describes the degree to which the two definitions are operationally equivalent. As would be expected from Fig. 1, the "errors" which form the basis of the Comment essentially disappear.

The Hinze and Jaffé conversion formula (5) was given (but not used) in Ref. 2. It provides a reasonable set of *electronegativity differences* even when using the Mulliken ground-state electronegativity scale.

In addition, it is important to note that the small differences between ground-state electronegativities and Pauling electronegativities cannot be taken as a measure of the "error" expected in the calculation of the ground-state electronegativities of fractionally charged elements. This error is determined primarily by errors in interpolating the ionization potentials and electron affinities along isoelectronic sequences, and by errors in the measurement of the electron affinities.

In setting up his electronegativity scale, Pauling implicitly associates a particular valence state with each of the elements. This is the valence state involved in the bond whose energy determines the Pauling electronegativity of that element. The conversion formula (5) attempts to relate the Mulliken electronegativities of these valence states to those of Pauling. Conventionally, the Mulliken-Jaffé electronegativity scale is based on those valence states which most closely represent the electron structure of the molecular bonds used by Pauling in establishing his scale. However, since the Mulliken valence-state electronegativities for fractionally charged elements are largely unknown, it is necessary, and fortunately possible, to define an electronegativity scale based on Mulliken ground-state electronegativities of both integrally and fractionally charged elements. This will be demonstrated shortly [Eq. (6) and Fig. 3].

An electronegativity scale based on valence states is theoretically more satisfying than one based only on ground states. However, it is difficult to identify the proper valence states for many of the elements. In establishing the connection (5) between the Mulliken valence state and Pauling electronegativity scales, Hinze and Jaffé[6] were able to use only eleven elements. By contrast, the ground-state electronegativity scale has the advantage that there is no arbitrariness in the choice of valence states, and electronegativity values are available for *all* elements.[2]

It is amusing to note that the ground-state electronegativities correlate more strongly with Pauling's than do the valence-state electronegativities, as can be seen by comparing the extent of the scatter present in Figs. 1 and 2.

TABLE I. Comparison of the Mulliken ground-state electronegativities given in Ref. 2 with those of Pauling. The ground-state electronegativities, which have been converted to the Pauling units in the third column, are compared with Pauling's electronegativity values given in the fourth column. The difference is noted in the fifth column. Values in parentheses are taken from the Comment and are included for comparison. Equation (3) has been used to convert the ground-state electronegativities which are measured in units of MJ/mole to Pauling units. The Comment inappropriately used Eq. (5) for the conversion and incorrectly ascribed significance to the absolute values obtained rather than to their differences. With reference to the singularly large deviation for hydrogen in the last column, we quote Pauling (Ref. 3) who noticed the same discrepancy: "It is seen that the values of [the electronegativity] x are closely proportional to those of the sum of the two energy quantities [IP and EA] except for hydrogen , which, with its unique electronic structure, might be expected to misbehave." The electronegativities in the tables are given to two decimal places only for purposes of comparison with the Comment. This reply adopts Pauling's view of the accuracy of his own electronegativities (Ref. 3): "These values [electronegativities] are given only to one decimal place on the scale; it is my opinion that this is the limit of their reliability."

	χ_{GS} (MJ/mole) Ref. 2	χ_{GS} (Pauling units) Ref. 2 (Ref. 1)	χ_{P} (Pauling units) Pauling	$\chi_{\mathrm{GS}}-\chi_{\mathrm{P}}$ (Pauling units) Ref. 2 (Ref. 1)
H	0.69	2.93 (2.21)	2.20	0.73 (0.01)
C	0.60	2.57 (1.90)	2.55	0.02 (−0.65)
N	0.67	2.84 (2.14)	3.04	−0.20 (−0.90)
O	0.73	3.07 (2.36)	3.46	−0.39 (−1.10)
F	1.00	4.19 (3.30)	3.98	0.21 (−0.68)
Cl	0.80	3.36 (2.60)	3.16	0.20 (−0.56)
Br	0.73	3.09 (2.36)	2.96	0.13 (−0.60)
I	0.65	2.76 (2.08)	2.66	0.10 (−0.58)
Ne	1.03	4.27 (3.41)	4.26	0.01 (−0.85)

TABLE II. Corrected version of Table I of the Comment. This table is identical to Table I of the Comment except that the proper conversion formula for comparing absolute values of electronegativity is used. Numbers in parentheses are taken from the Comment. The ratio listed in the last column is much closer to zero then Liebman and Huheey claim. They also erroneously claim that this ratio is a measure of the error made in computing electronegativities of fractionally charged atoms (see the text).

	χ_{LZ} χ_{LZ_+} Ref. 2 (Ref. 1)	(Average, $\bar{\chi}$) $(\chi_{\mathrm{P}},\chi_{\mathrm{S}},\chi_{\mathrm{AR}},\chi_{\mathrm{MJ}})$ Ref. 1	Difference $\bar{\chi}-\chi_{\mathrm{LZ}}$ This paper	Difference $\chi_{\mathrm{LZ}_+}-\chi_{\mathrm{LZ}}$ This paper	Ratio $\frac{\bar{\chi}-\chi_{\mathrm{LZ}}}{\chi_{\mathrm{LZ}_+}-\chi_{\mathrm{LZ}}}$ This paper (Ref. 1)
Li	1.28 (0.82)	(0.91±0.06)	−0.37		
	2.39 (1.76)			1.11	−0.34 (0.10)
Be	1.45 (0.96)	(1.51±0.08)	0.06		
	2.92 (2.22)			1.48	0.04 (0.44)
B	1.78 (1.24)	(1.94±0.09)	0.16		
	3.40 (2.64)			1.62	0.10 (0.50)
C	2.57 (1.90)	(2.50±0.03)	−0.07		
	4.33 (3.44)			1.76	−0.04 (0.39)
N	2.84 (2.14)	(3.01±0.06)	0.17		
	4.82 (3.86)			1.97	0.08 (0.51)
O	3.07 (2.36)	(3.47±0.02)	0.40		
	5.20 (4.18)			2.13	0.19 (0.61)
F	4.19 (3.30)	(3.98±0.08)	−0.21		
	6.61 (5.36)			2.42	−0.09 (0.33)
Cl	3.36 (2.60)	(3.06±0.18)	−0.30		
	4.97 (3.96)			1.60	−0.19 (0.33)
Br	3.09 (2.36)	(2.82±0.15)	−0.27		
	4.47 (3.54)			1.39	−0.19 (0.39)
I	2.76 (2.08)	(2.47±0.16)	−0.29		
	3.97 (3.12)			1.21	−0.24 (0.38)

However, the valence-state electronegativities of the eleven elements picked by Hinze and Jaffé do indeed show a stronger correlation to Pauling's values than the ground-state electronegativities of these same elements. Presumably, therefore, the valence-state electronegativity scale and the Pauling electronegativity scale are operationally equivalent as originally suggested by Hinze and Jaffé.[6]

In spite of the difficulties in assigning valence-state electronegativities, Ref. 2 advocates the use of valence-state electronegativities for both integrally and fractionally charged elements.[13] The use and interpretation of valence-state electronegativities is not controversial. Figures 1 and 2 have established that the ground-state and valence-state electronegativity scales are both operationally equivalent to the Pauling scale and so are operationally equivalent to each other. Therefore, it is still correct, and certainly more convenient, to use the Mulliken ground-state electronegativity scale rather than one based on valence states.

The equivalence between the valence-state and ground-state electronegativity scales, which has been demonstrated for neutral atoms, holds for charged atoms as well. More explicitly, it will be shown here that ground-state electronegativities and valence-state electronegativities for both neutral and charged atoms are correlated by a single linear function that is independent of the net atomic charge, i.e.,

$$\chi_{\mathrm{VS}}=\alpha\chi_{\mathrm{GS}}+\beta\ , \tag{6}$$

where α and β do not depend on the net charge of the atom. Figure 3 demonstrates the remarkable fact that this linear relation holds for neutral atoms and ions with charge one. Therefore, the same relation is expected to hold for atoms with fractional net charges between zero and one.[14]

A best linear fit to the data shown in Fig. 3 gives

$$\alpha=1.01,\ \beta=0.12\ . \tag{7}$$

Since α is so close to one, ground-state electronegativity differences are essentially equal to valence-state electronegativity differences.

IV. SUMMARY

The comments by Liebman and Huheey are primarily confusing for two reasons. First, they judge the correctness of the Mulliken ground-state electronegativities given in Ref. 2 by converting them to the Pauling electronega-

TABLE III. Same as Table II, except that the uninterpretable average $\bar{\chi}$ of four electronegativities used in the Comment is replaced by Pauling's electronegativity χ_P, as tabulated in Ref. 7.

	χ_{LZ} χ_{LZ_+} Ref. 2 (Ref. 1)	Pauling χ χ_P	Difference $\chi_P - \chi_{LZ}$ This paper	Difference $\chi_{LZ_+} - \chi_{LZ}$ This paper	Ratio $\frac{\chi_P - \chi_{LZ}}{\chi_{LZ_+} - \chi_{LZ}}$ This paper (Ref. 1)
Li	1.28 (0.82)	0.98	−0.30		
	2.39 (1.76)			1.11	−0.27 (0.10)
Be	1.45 (0.96)	1.57	0.13		
	2.93 (2.22)			1.48	0.08 (0.44)
B	1.78 (1.24)	2.04	0.26		
	3.40 (2.64)			1.62	0.16 (0.50)
C	2.57 (1.90)	2.55	−0.02		
	4.33 (3.44)			1.76	−0.01 (0.39)
N	2.84 (2.14)	3.04	0.20		
	4.82 (3.86)			1.97	0.10 (0.51)
O	3.07 (2.36)	3.44	0.37		
	5.20 (4.18)			2.13	0.17 (0.61)
F	4.19 (3.30)	3.98	−0.21		
	6.61 (5.36)			2.42	−0.09 (0.33)
Cl	3.36 (2.60)	3.16	−0.20		
	4.97 (3.96)			1.60	−0.13 (0.33)
Br	3.09 (2.36)	2.96	−0.13		
	4.47 (3.54)			1.39	−0.09 (0.39)
I	2.76 (2.08)	2.66	−0.10		
	3.97 (3.12)			1.21	−0.08 (0.38)

tivity scale and comparing the resulting values with those of Pauling. The large differences in electronegativity values they observe lead them to conclude that the Mulliken ground-state electronegativities are "incorrect."

This Reply points out that there are several equally valid ways of defining electronegativity, each definition summarizing different but correlated chemical effects. It is incorrect to say that Mulliken ground-state electronegativities found from ionization potentials and electron affinities are in error because they do not agree with the Pauling electronegativities that are derived from molecular bond energies.

The Mulliken ground-state electronegativities assigned to fractionally charged atoms in Ref. 2 would be in error only if the ionization potential or electron affinities had been incorrectly computed. The calculation of these quantities is correct, however, and is not challenged in the Comment. The Comment also does not claim that the chemical significance of Mulliken ground-state electronegativities was incorrectly interpreted.

A correlation between electronegativities derived from different definitions may be used to establish their operational equivalence. This reply has demonstrated that despite differences in definition, the Mulliken ground-state electronegativities define a scale that is operationally equivalent to the Pauling scale for neutral atoms. It has also been shown that the Mulliken ground-state electronegativity scale for both neutral and charged atoms is operationally equivalent to one based on valence states. A single electronegativity scale based on Mulliken ground-state electronegativities may therefore be used for neutral atoms, ions, and fractionally charged atoms, as originally implied in Ref. 2.

By using a conversion formula appropriate for the valence-state electronegativity scale [Eq. (5)], Liebman and Huheey missed the strong empirical correlation between ground-state and Pauling electronegativities [Fig. 1 and Eq. (3)]. When Mulliken ground-state electronegativities are correctly converted to Pauling units, the large discrepancies which form the basis of the Comment by Liebman and Huheey essentially disappear (Table I). In addition, by incorrectly attributing significance to the magnitudes of electronegativities rather than just to their differences, Liebman and Huheey have discovered "errors" of their own making.

The second major source of confusion is the contention of the Comment that the electronegativities in Ref. 2 are incorrect because they were not computed for non-ground-state valence states. Apart from the fact that ground-state electronegativities may be used to define a consistent electronegativity scale, this criticism is misplaced because it does not acknowledge that there is an electronegativity for each valence state, including the ground state, and that the computation of the ground-

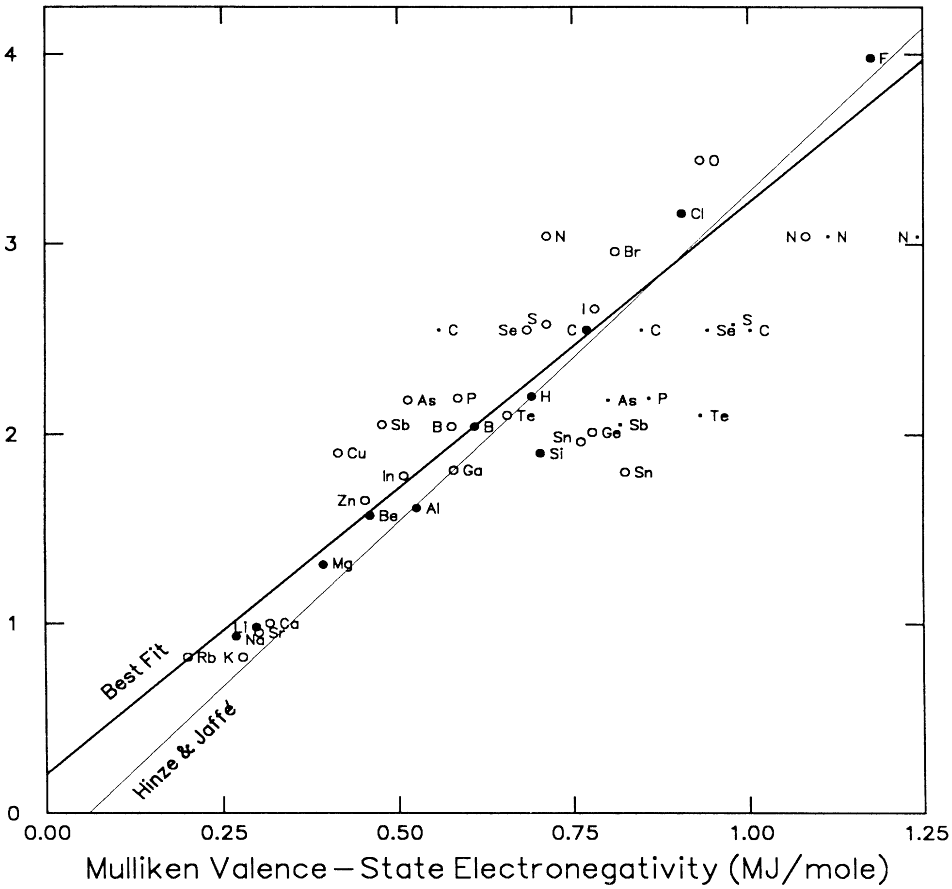

FIG. 2. Scatter plot demonstrating that Pauling electronegativities and Mulliken valence-state electronegativities are linearly correlated. The closed circles indicate the elements used by Hinze and Jaffé (Ref. 6) to establish the conversion formula [Eq. (5)] represented by the straight line bearing their names. The open circles and dots represent additional valence states tabulated in Huheey's book (Ref. 7). Only the solid and open circles were used in establishing the best fit.

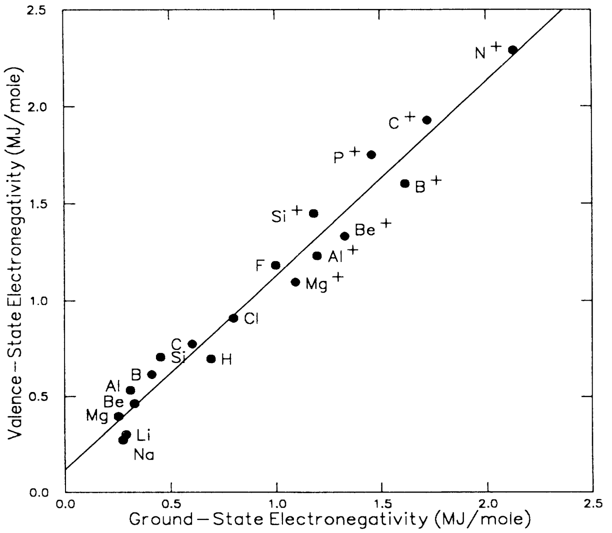

FIG. 3. Scatter plot demonstrating the universal linear correlation between ground-state electronegativities and valence-state electronegativities for both neutral atoms and positive ions.

state electronegativities serves as a convenient starting point for the computation of other valence-state electronegativities. In addition, the criticism is not appropriate because the Comment was written as if the significance of non-ground-state valence states was not recognized and discussed in detail in Ref. 2.

This reply has addressed the issues involved in assigning electronegativities to neutral atoms, ions, and fractionally charged atoms. It is based on the observation that any two definitions of electronegativity which lead to linearly related electronegativity values are operationally equivalent. The ground-state electronegativity scale has been shown to be operationally equivalent to the empirically based Pauling electronegativity scale as well as to the theoretically motivated Mulliken valence-state electronegativity scale. In contrast with the Pauling scale, the ground-state electronegativity scale can be extended to ions and fractionally charged atoms. The uncertainties in choosing the proper valence states for an atom in a molecule, which complicate the interpretation of Mulliken valence-state electronegativities, do not affect the interpretation of ground-state electronegativities. There are sufficient data to assign ground-state electronegativity values to all neutral atoms, most ions, and all fractionally charged atoms; this is not the case for Mulliken valence-state electronegativities. Therefore, the only consistent and comprehensive electronegativity scale currently available is based on ground-state electronegativities.

Note added in proof. The "note added in proof" of Liebman and Huheey states that in some cases the ordering of ground-state electronegativities whose numerical values are close is not the same as the ordering of the corresponding electronegativities given by other definitions. However, it is surprising that they have chosen oxygen and nitrogen for two of their examples. They did not include valence-state electronegativities for these elements in their Table I and state in a footnote to the Table: "Since nitrogen and oxygen do not form exact *spn* (with *n* an integer) the definition of the valence state (particularly the hybridization) is especially difficult for these elements." Equally surprising is their example of the noble gasses, exceptional cases, for which Mulliken non-ground-state valence electronegativities do not exist. Their remaining two examples are clearly illustrated in Fig. 1 of this Reply where the correlation between Pauling electronegativities and Mulliken ground-state electronegativities is given. Figure 2 of this Reply illustrates that similar inversions can be found for Pauling electronegativities and Mulliken valence-state electronegativities.

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[5] The averaging of electronegativity values obtained from several definitions implies that there is one "ideal" concept of electronegativity to which each definition imperfectly aspires. This view is not correct; each definition captures different but correlated aspects of chemistry.

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[11] The parameters a and b in the Comment correspond to χ and χ' in Ref. 2.

[12] The formula first posited by Hinze and Jaffé and used by Liebman and Huheey in their Comment.

[13] Note that Pauling's definition of electronegativity cannot currently be extended to fractionally charge elements since it is empirically based.

[14] In fact, arguments based on isoelectronic sequences of neutral atoms and ions can be used to show that atoms with net fractional charge between zero and one interpolate between these states.