QUANTUM-THERMODYNAMIC DEFINITION OF ELECTRONEGATIVITY*

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(1) Introduction.—Rigorous definitions of electronegativity of atoms, neutral or ionized, and of atomic orbitals are given. The definitions are consistent with the rules of the statistics of ensembles and the quantum-mechanical picture of atomic structure. The definitions have been extended to atoms in a molecule and to atoms in a solid. The extensions, however, will be presented in future communications.

The concept of electronegativity, "the power of an atom in a molecule to attract electrons to itself," has been found to be a useful tool for the correlation of a vast field of chemical knowledge and experience. But in spite of the great amount of literature on the subject, no rigorous definition of electronegativity has been suggested. The lack of definition has resulted in some confusion with respect to both the physical concept represented by electronegativity and the units of electronegativity.

In the present communication, a free atom or a free ion is regarded as a thermodynamic system, and the electronegativity of such a system is identified with the negative of its electrochemical potential.

The electrochemical potential of a component in a phase may be evaluated by means of the theory of statistical ensembles. This theory, whether related to classical or quantum mechanics, applies to thermodynamic systems of any size. Consequently, it is possible to find ensemble (thermodynamic) properties, such as the electrochemical potential, even of an atom representative of an ensemble of one-atom members. If the center of mass of each atom is fixed in space, both the one-atom members and the one-atom thermodynamic system representative of the ensemble may be regarded as open systems having one independent component, namely, electrons.

Even when all the mechanical properties of an atom, such as the energy eigenvalues and the number of electrons, assume only discrete values, the thermodynamic properties of the one-atom system representative of the ensemble, such as the energy $E$ and the number of electrons $n$, assume continuous values. Each of these properties may be expressed as a continuous function of two independent thermodynamic variables.

The electrochemical potential $\mu$ is defined as the partial derivative of $E$ with respect to $n$ at constant entropy. This derivative must be evaluated for the ensemble passing through equilibrium states because otherwise it is indeterminate. This fact in turn implies that in any calculation of $\mu$, two independent thermodynamic variables, say, $n$ and temperature $T$, must be considered even if the interest is in results at $0^\circ$K. For example, if $\mu$ is computed as the derivative mentioned above, in order to vary $n$ at constant entropy while the ensemble
passes through equilibrium states, $T$ must be varied. Hence, both $n$ and $T$ must be retained in $E$.

In view of these remarks, this paper is organized as follows. First, a brief review of the statistics of grand canonical ensembles is given. Second, this statistics is applied to an ensemble of one-atom members. The procedure for the calculation of the electrochemical potential is thus established. Third, electronegativity is defined as the negative of the electrochemical potential. For a neutral atom at $0^\circ K$, this definition yields exact results which are identical to those of Mulliken. Finally, it is shown that when the electronic structure of the atom is described by the Hartree-Fock approximation, that is when the electrons are treated as an ideal substance, an orbital electronegativity can be defined.

It should be noted that since the electrochemical potential is interpreted as the escaping tendency (the opposite of the power to attract) of a component from a thermodynamic system, it is reasonable to use the negative of this potential as a measure of electronegativity.

(2) Statistics of Grand Canonical Ensembles.—Consider an ensemble of identical members, namely, members which have identical possible energy eigenstates. Suppose that the ensemble is in thermodynamic equilibrium, at $T$, and that its members can exchange energy and matter with the members of a reservoir. Such an ensemble is defined as a grand canonical ensemble.

For present purposes, the members of the ensemble are specified by the following conditions: (a) each member has only one independent component; (b) the energy eigenstates of each member are $G_1, G_2, \ldots, G_i, \ldots$; and (c) each energy eigenstate $G_1, G_2, \ldots, G_p, \ldots$ is occupied by a number $n_1, n_2, \ldots n_p, \ldots$ of particles of the component and has an energy $E_1, E_2, \ldots E_p, \ldots$, respectively. Here, separate symbols for the energy and the occupation number are used for each energy eigenstate, even though more than one of these symbols may represent the same number. For example, a $g$-fold degenerate state is counted as $g$ separate states.

When the laws of thermodynamics are applied to the ensemble and the reservoir, it is found that the fraction $x_i$ of members at the energy eigenstate $G_i$, the probability $x_i$ that a member is at the state $G_i$, is given by the relation

$$x_i = \frac{\exp[(n_i \mu - E_i)/kT]}{\sum_i \exp[(n_i \mu - E_i)/kT]}, \tag{1}$$

where $\mu$ is the electrochemical potential of the component in the ensemble and in the reservoir, and $k$ is Boltzmann’s constant. Note that at $T = 0$, $x_i$ can be computed only as a limit.

By virtue of equation (1), it follows that, statistically, the average number $n$ of particles representative of the ensemble is given by the relation

$$n = \sum_i n_i x_i = \frac{\sum_i n_i \exp[(n_i \mu - E_i)/kT]}{\sum_i \exp[(n_i \mu - E_i)/kT]} \tag{2}.$$
Equation (2) indicates that \( n \) is a continuous function of the continuous variables \( \mu \) and \( T \). Conversely, equation (2) can be solved for the continuous function \( \mu(n, T) \) of the continuous variables \( n \) and \( T \). The range of \( n \) is the same as that of the discrete values \( n_i \).

It also follows from equation (1) that the average energy \( E \) of the ensemble is given by the relation

\[
E = \sum_i E_i x_i. \tag{3}
\]

This energy can be thought of as a continuous function of any two of the continuous variables \( n, \mu \), and \( T \), and it is related to the electrochemical potential by the expression

\[
\mu = \frac{\partial E}{\partial n} \text{ at constant entropy.} \tag{4}
\]

The derivation of the last relation is given in reference 9.

3) Electrochemical Potential of Atoms and Atomic Ions.—Consider the special ensemble of identical, one-atom members of atomic number \( Z \). Suppose that each member may exchange energy and only electrons with a reservoir. In thermodynamic equilibrium, this thermodynamic system constitutes a grand canonical ensemble of one-component (electron) members.

To proceed with the statistical analysis of the system, suppose first that only the ground state of the singly charged negative ion of the atomic species exists. Thus, the possible energy eigenstates of each one-atom member of the ensemble are as follows:

(a) Ground states: Figure 1 shows schematically the possible occupation numbers \( n_i \),

\[
n_i = 0, 1, 2, \ldots, Z, Z + 1, \tag{5}
\]

and the corresponding energies \( E_i \) of the ground states of the neutral atom and all the positive and negative ions. It is seen from the figure that as the electron occupation number increases from zero (fully ionized atom) to \( Z + 1 \) (singly

<table>
<thead>
<tr>
<th>Eigenstate ( G_i )</th>
<th>Occupation number ( n_i )</th>
<th>Energy ( E_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G_0 )</td>
<td>0</td>
<td>( E_0 ) ( 1 )</td>
</tr>
<tr>
<td>( G_1 )</td>
<td>1</td>
<td>( E_1 ) ( 1 )</td>
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<tr>
<td>( G_{Z+1} )</td>
<td>( Z+1 )</td>
<td>( E_{Z+1} ) ( 1 )</td>
</tr>
<tr>
<td>( G_Z )</td>
<td>( Z )</td>
<td>( E_Z ) ( 0 )</td>
</tr>
<tr>
<td>( G_{Z+1} )</td>
<td>( Z+1 )</td>
<td>( E_{Z+1} ) ( -A )</td>
</tr>
</tbody>
</table>

Positive ions

Neutral atom

Negative atom

FIG. 1.—Schematic of ground states of the neutral atom and all the positive and negative ions of an atom forming only singly charged negative ions. No degeneracies are shown.
charged negative ion), the energies of the corresponding ground states satisfy the relations

\[ E_0 > E_1 > \ldots > E_{z-1} > E_z > E_{z+1}. \]  

If the arbitrary zero energy reference level is set at the energy \( E_z \) of the neutral atom, relation (6) may be written in the form

\[ I_z > I_{z-1} > \ldots > I_1 > 0 > -A_1, \]  

where \( I_i \) and \( A_i \) are the \( i \)th ionization energy and electron affinity of the atom, respectively.

(b) **Excited states:** To each occupation number \( n_i \) smaller than or equal to \( Z \), there corresponds an infinite number of excited states. Let the energy of each such state be denoted by \( E_{ij} \). Each energy \( E_{ij} \) is greater than the energy \( E_t \) of the corresponding ground state.

In terms of the above energy eigenstates, the average number \( n \) of electrons representative of the ensemble is given by the relation

\[ n = \frac{\sum_{i=0}^{Z+1} n_i \exp \left[ (n_i \mu - E_i)/kT \right] + \sum_{i=0}^{Z} \sum_{j} n_i \exp \left[ (n_i \mu - E_{ij})/kT \right]}{\sum_{i=0}^{Z+1} \exp \left[ (n_i \mu - E_i)/kT \right] + \sum_{i=0}^{Z} \sum_{j} \exp \left[ (n_i \mu - E_{ij})/kT \right]}. \]  

It follows from equation (8) that the number of electrons of the atom, viewed as a thermodynamic system, may assume any value between 0 and \( Z + 1 \), even though the occupation numbers \( n_i \) assume only discrete values. Moreover, for given values \( n \) and \( T \), equation (8) can be solved for \( \mu \). Although the general solution is numerically tedious, some general results can be readily established:

(i) If the ensemble is representative of either the fully ionized atom \( (n = 0) \) or the singly charged negative ion \( (n = Z + 1) \), equation (8) yields

\[ \mu = -\infty \quad \text{for } n = 0, \]  

or

\[ \mu = +\infty \quad \text{for } n = Z + 1, \]  

respectively, for all values of \( T \). These extreme values of \( \mu \) are as expected, since for \( n = 0 \) and \( Z + 1 \) the variations \( dn \) of the electron component are restricted to be only positive and negative, respectively.\(^{10}\)

(ii) For values of \( n \) in the range

\[ Z < n \leq Z + 1, \]  

\( \mu \) is positive. For all other values of \( n \), the electrochemical potential is negative. These facts can be readily verified by substitution of a nonnegative value of \( \mu \) in equation (8).

(iii) If the ensemble is representative of a neutral atom, \( n = Z \). For this value of \( n \) and in the limit of small temperatures \( (T \) approximately equals \( 0^\circ K) \), equation (8) yields
\[ \mu = - (I_1 + A_3)/2 + kT \ln g_{n-1} \quad \text{for } n = Z, \text{ and } T \to 0, \] (12)

where \( g_{n-1} \) is the degeneracy of the state \( G_{n-1} \). Equation (12) is a special case of a more general result discussed below.

(iv) If the ensemble is representative of a positive ion with an integral number \( n \) of electrons, \( n = \sigma \). For such a value of \( n \), equation (8) may be written in the equivalent form:

\[
\sum_{i=0}^{z-1} (\sigma - n_i) \exp \left[ \frac{(\sigma \mu - E_i)/kT}{\sum_{i=0}^{z-1} (\sigma - n_i) \exp \left[ (n_i \mu - E_{i})/kT \right]} \right] = \sum_{i=\sigma+1}^{z+1} (n_i - \sigma) \exp \left[ (n_i \mu - E_i)/kT \right] + \sum_{i=0}^{z} (n_i - \sigma) \exp \left[ (n_i \mu - E_{i})/kT \right]. \] (13)

For \( \mu \) negative and in the limit of small temperatures, the first sum on either side of equation (13) is much greater than the second. Hence, a good approximation to equation (13) is given by the relation

\[
\sum_{i=0}^{z-1} (\sigma - n_i) \exp \left[ (n_i \mu - E_i)/kT \right] = \sum_{i=\sigma+1}^{z+1} (n_i - \sigma) \exp \left[ (n_i \mu - E_i)/kT \right]
\] for \( n = \sigma \) and \( T \to 0. \) (14)

For different ranges of negative values of \( \mu \), the exponents \( n_i \mu - E_i \) on either side of equation (14) can be ordered. Given a range of values of \( \mu \), suppose that the largest exponents are \( l \mu - E_l \) and \( r \mu - E_r \) on the left- and right-hand side, respectively, where

\[ l \leq \sigma - 1 \quad \text{and} \quad r \geq \sigma + 1. \] (15)

It follows that, in the limit of small temperatures, equation (14) can be approximated by the simple expression

\[ g_l (\sigma - l) \exp \left[ (l \mu - E_l)/kT \right] = g_r (r - \sigma) \exp \left[ (r \mu - E_r)/kT \right], \] (16)

where \( g_l \) and \( g_r \) are the degeneracies of the states \( G_l \) and \( G_r \), respectively. The last expression is satisfied for the value of \( \mu \) given by the relation

\[
\mu = - [(E_r - E_l) + kT \ln \frac{g_l (\sigma - l)}{g_r (r - \sigma)}/(r - l)]
\] for \( n = \sigma \), and \( T \to 0. \) (17)

This value of \( \mu \) is acceptable if it is within the range of values assumed for the ordering of the exponents, namely, within the range which resulted in approximate equation (16). Otherwise, another range of \( \mu \) and different values of \( l \) and \( r \) must be considered.

For \( n \) equal to or smaller than \( Z - 1 \), consideration of the ionization energies of atoms as specified above results in values of \( \mu \) which are much smaller than that for \( n = Z \). For practical purposes, it is convenient (but not necessary) to assume

\[ \mu = - \infty \quad \text{for } n \leq Z - 1 \text{ and all } T. \] (18)

The preceding statistical analysis can be readily applied to atoms which either
can form both singly and doubly charged negative ions or cannot form negative ions. Thus, for example, for atoms which form both singly and doubly charged negative ions, \( n_t \) ranges from 0 to \( Z + 2 \), it is found that for \( n = Z \) a possible value of \( \mu \) is given by the relation

\[
\mu = - \left( I_2 + A_2 \right)/4 \quad \text{for} \quad n = Z \quad \text{and} \quad T = 0,
\]

provided that

\[
3 I_2 < 4I_1 + A_2, \quad \text{and} \quad 4A_1 < 3A_2 - I_2.
\]

4. Electronegativity of Atoms and Atomic Ions.—The electronegativity of a neutral or charged atomic species is defined here as the negative of the electrochemical potential of the species viewed as a one-component member of a grand canonical ensemble. Thus, the electronegativity \( x(n, T) \) is given by the relation

\[
x(n, T) = - \mu,
\]

and is a continuous function of the continuous variables \( n \) and \( T \). Note that when the zero energy level is set at the level of the ground state of the neutral atom, the value of the electrochemical potential equals that of the chemical potential. For this energy reference level, the electronegativity equals the negative of the chemical potential. Note also that \( x \) can be expressed as a continuous function of another pair of continuous thermodynamic variables, say, entropy and \( n \).

Qualitatively, this definition of electronegativity is consistent with heuristic descriptions given previously. The negative of \( \mu \), the negative of the escaping tendency, represents a power to attract. A power to attract is the notion associated with electronegativity. Moreover, equality of the electrochemical potentials of a component in two different phases implies that there is no flow of this component between the two phases. In direct analogy, equality of electronegativities of two atoms implies that there is no flow of electronic charge from one atom to the other.

Quantitatively, for atoms which can form singly charged negative ions, it is seen from equations (12) and (21) that the exact value of the electronegativity \( x(Z, 0) \) of the neutral atom is given by the relation

\[
x(Z, 0) = (I_1 + A_1)/2.
\]

This value is identical to the approximate value recommended by Mulliken.\(^4\) Also, the exact value of the electronegativity given by the negative of equation (10) was suggested by Mulliken\(^4\) without reference to the restrictions represented by relations (20).

5. Orbital Electronegativity.—The discussion in section 3 and the definition of electronegativity in section 4 are presented without any reference to the procedure employed for the determination of the possible energy eigenstates of the members of the ensemble. Consideration of the approximate methods used for the calculation of the energy eigenvalues leads to the concept of orbital electronegativity.

To see this point clearly, consider a \( Z \)-electron atom. The quantum-mechan-
ical analysis of the electronic structure of this atom is very difficult. The difficulty is avoided if the electrons are treated as an ideal substance, that is, the Z-electron Hamiltonian operator is reduced to an approximate sum of Z separable, one-electron Hamiltonian operators. The reduction can be made by means of different approximate methods. One of these is the Hartree-Fock method.

The Hartree-Fock one-electron operator defines an energy eigenvalue problem. Each eigenfunction of this operator, one-electron orbital, can accommodate at most two electrons with opposite spins. When the orbital, is occupied by an electron with a given spin, it is called a spin-orbital. The negative of each eigenvalue is interpreted as an ionization energy. This interpretation is based on the assumption that the extraction of the electron from the corresponding orbital does not perturb the eigenstates of the other electrons, and it is known as Koopmans’ theorem. Finally, the energy of a given state of the atom is given approximately by the sum of the energies of the occupied spin-orbitals.

This way of thinking about the atom has the following implications for an atom which forms only singly charged negative ions. (a) The energies \( I_1 \) and \( A_1 \) of the atom may be thought of as the ionization energy and the electron affinity of a valence orbital, respectively. (b) Variations of the charge of the atom, regarded as a thermodynamic system, in the range

\[
Z - 1 \leq n \leq Z + 1
\]

may be thought of as occurring because of continuous variations of the charge in the valence orbital. (c) For values of \( n \) in the range represented by relations (23), the energy \( E(n, T) \) (Eq. 3) is a function of the charge in the valence orbital only. This statement is justified by Koopmans’ theorem. (d) Suppose that the average charge in the valence orbital is represented by \( q \), so that

\[
q = +e \text{ for } n = Z - 1, \quad q = 0 \text{ for } n = Z, \quad \text{and } q = -e \text{ for } n = Z + 1,
\]

where \( e \) is the electronic charge. At zero temperature, the energy and electrochemical potential of the atom may be thought of as the energy \( \epsilon_0(q) \) and the electrochemical potential \( \mu_0(q) \) per unit charge of the valence orbital, respectively. From the results of section 4, it is readily verified that for

\[
q = e, \quad \epsilon_0(q) = I_1, \quad \mu_0(q) = -\infty,
\]

\[
q = 0, \quad \epsilon_0(q) = 0, \quad \mu_0(q) = -(I_1 + A_1)/2e,
\]

\[
q = -e, \quad \epsilon_0(q) = -A_1, \quad \mu_0(q) = +\infty.
\]

These values suggest that \( \epsilon_0(q) \) and \( \mu_0(q) \) may be represented by the approximate continuous functions given by the relations

\[
\epsilon_0(q) = \frac{I_1 + A_1}{2e} q + \frac{I_1 - A_1}{2} \left[ 1 - \left( 1 - \frac{q^2}{e^2} \right)^{1/2} \right],
\]

and

\[
\mu_0(q) = -\frac{d\epsilon_0(q)}{dq} = -\frac{I_1 + A_1}{2e} - \frac{I_1 - A_1}{2} \frac{(q/e)}{\left[ 1 - (q/e)^2 \right]^{1/2}}.
\]
(e) It follows that, at zero temperature, the electronegativity of the atom may be thought of as an orbital electronegativity \( x_0(q) \) given by the approximate relation

\[
x_0(q) = \frac{d\varepsilon_0}{dq} = \frac{I_1 + A_1}{2e} + \frac{I_1 - A_1}{2} \frac{q/e}{[1 - (q/e)^2]^{1/2}} \tag{27}
\]

(f) Similar statements can be made about other types of atoms.

Expressions somewhat analogous to those represented by equations (25) and (27) have been introduced heuristically by other authors who expressed doubts about the validity of the assumption that both \( \varepsilon_0(q) \) and \( x_0(q) \) are continuous functions of the continuous variable \( q \). In view of the present work, it is seen that orbital electronegativity is obtained from basic quantum-thermodynamic arguments and that, indeed, \( \varepsilon_0(q) \) and \( x_0(q) \) are continuous functions of the continuous thermodynamic variable \( q \).

The preceding approach to the definition of electronegativity has been extended to atoms in molecules and solids. The results will be presented in future communications.

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