QUANTUM-THERMODYNAMIC MEANING OF
ELECTRONEGATIVITY AND WORK FUNCTION

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ABSTRACT

The purpose of this paper is to discuss the relation between surface orbital electronegativity and work function, both from the standpoint of thermodynamics and that of quantum mechanics.

First, it is shown that the electronic structure of crystals can be described by means of spin-orbitals which are localized around individual lattice sites. Second, electronegativity is related to the chemical potential of an electron in a spin-orbital. Third, it is shown that the work function of a uniform surface equals the neutral orbital electronegativity of a spin-orbital localized around a surface atom.

INTRODUCTION

In previous publications by Steiner and Gyftopoulos,[1-3] emission phenomena, occurring at metallic surfaces, are analyzed in terms of surface atoms and their orbital electronegativity. For example, in reference 1 the view is advanced that electrons, emitted thermionically from a pure uniform surface of a crystal, originate from a " valence orbital" of an " atom on the surface. " It is assumed that the shape, the ionization energy, the electron affinity, and the excitation energies of this orbital are precisely defined, although not necessarily spectroscopically observable, and that they are determined by the many-body interactions of the crystal. On the basis of this picture, it is concluded that the work function of the surface must equal the neutral orbital electronegativity of the valence orbital of the surface atom.

This way of thinking about a crystal and its surface raises two questions. The first relates to the validity of viewing the electronic structure of a crystal in terms of orbitals which are associated with individual lattice sites, such as a valence orbital of a surface atom. It is customary to think of the electrons as belonging to the crystal as a whole and, therefore, it is not obvious that electrons can be assigned to, localized around, individual lattice sites.

The second is a relatively old question. It refers to the meaning of electronegativity. This quantity has been found useful in many chemical studies and yet it has not been given a rigorous definition.

The purpose of the present communication is to discuss the preceding two questions, in the context of the one-electron approximation for the electronic structure of many-electron systems. It is shown that the picture of localized orbitals is valid, and that electronegativity equals the negative of the chemical potential of an electron in an orbital.

The paper is organized as follows. First, the procedure for the derivation of the localized orbitals is discussed. These orbitals are shown to provide a description of the electronic structure of crystals which is entirely equivalent to the well known quantum-mechanical picture of electrons in metals. Second, the work of the authors on the identification of electronegativity[4] with the chemical potential is summarized. Third, it is shown that the work function of a pure uniform surface equals the orbital electronegativity of a surface atom.

LOCALIZED SPIN-ORBITALS FOR CRYSTAL LATTICES

The equivalence between the descriptions of the electronic structure of crystals by means of either nonlocalized, band structure theory, or localized spin-orbitals is best understood through a brief review of procedures employed for the analysis of any N-electron system.

Quantum-mechanically, the analysis of the energy eigenstates of the electronic structure of N-electron systems is very difficult. To avoid the difficulty, the electrons are treated as an ideal substance. In other words, the N-electron Hamiltonian operator is reduced to a sum of N separable one-electron Hamiltonian operators. Various methods are used for the reduction. Differences between methods arise from the degree to which exchange and correlation effects are included in the one-electron potential energy. In this regard, all methods are approximate and not all methods are equally accurate.

A given one-electron Hamiltonian operator defines an energy eigenvalue problem. The eigenfunctions and eigenvalues of this operator can be more readily found than those of the complete N-electron operator. Each eigenfunction, one-electron orbital, of a system with more than one nucleus, is delocalized throughout the system and is given the same interpretation as, say, the eigenfunctions of the hydrogen atom. For example, the orbital can accommodate at most two electrons with opposite spins. The negative of the eigenvalue equals approximately the energy required to extract an electron from the orbital, and it represents an

ionization energy of the system. When the orbital is occupied by an electron with a given spin, it is called a spin-orbital. In many applications, a different orbital is used for each spin. In other words, each spin-orbital has its own spatial dependence.

By virtue of the ideal substance assumption, the eigenfunction ψ_N, for a given state of the system as a whole, should be given by the product of the occupied spin-orbitals. This, however, is not consistent with the symmetry rules of quantum mechanics.[5] For this reason ψ_N is represented by an antisymmetric, determinantal function of spin-orbitals, a Slater determinant.[6] The determinant is given by the relation

$$\psi_N = \frac{1}{(N!)^{1/2}} \begin{vmatrix} u_1(q_1) & u_2(q_1) & \cdot & \cdot & u_N(q_1) \\ u_1(q_2) & u_2(q_2) & \cdot & \cdot & u_N(q_2) \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ u_1(q_N) & u_2(q_N) & \cdot & \cdot & u_N(q_N) \end{vmatrix} \quad (1)$$

where q_j represents the coordinates and spin of the j-th electron, u_i is the i-th orbital, and $u_i(q_j)$ is the i-th spin-orbital occupied by the j-th electron.

In general, it is found that one-electron energies E_i, eigenvalues E_i, are in good agreement with experimentally observed ionization energies of the system (atom, molecule, or crystal). However, the sum of the E_i, the eigenvalue of ψ_N with respect to the sum of the N one-electron operators, is not in good agreement with the total energy of the system, namely the energy which would be derived from the exact ψ_N and the exact N-electron operator. Nevertheless, ψ_N in the form of Eq. 1 is often considered as an adequate approximation for the exact ψ_N.

For crystals, the one-electron results can also be described in terms of localized orbitals by means of the following procedure. Consider a crystal bounded by a uniform surface. Suppose that a relatively

accurate one-electron equation has been established, say, by the method suggested by Slater.[7] The one-electron eigenvalue problem may be written in the form

$$(H_o + H_1) u = E u, \qquad (2)$$

where H_o is the one-electron, spatially periodic, Hamiltonian operator that would be derived if the solid were imbedded in an infinite lattice, and H_1 is the one-electron operator which accounts for the perturbation introduced by the uniform surface. The spatial part of the eigenfunctions of Eq. 2 can be expanded into a series of Wannier functions[8] $a_n(r - R_s)$ associated with the operator H_o.[†] Thus the i-th eigenfunction is given by the relation[9]

$$u_i(\underline{r}) = \sum_s \sum_n U_{in}(\underline{R}_s) a_n(\underline{r} - \underline{R}_s), \qquad (3)$$

where $U_{in}(\underline{R}_s)$ is a constant, and the sums are over all lattice sites $\underline{R}_s$ and over all bands n. Mathematically, Eq. 3 is exact if an infinite number

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[†] Recall that the Block functions $b_n(\underline{k}, \underline{r})$ of the n-th band of the infinite crystal are given by the relation[10]

$$H_o b_n(\underline{k}, \underline{r}) = E_n(\underline{k}) b_n(\underline{k}, \underline{r}),$$

and that the Wannier functions $a_n(\underline{r} - \underline{R}_s)$ of the n-th band are determined by the expression

$$a_n(\underline{r} - \underline{R}_s) = N_L^{-1/2} \sum_k b_n(\underline{k}, \underline{r}) \exp(-i\underline{k} \cdot \underline{R}_s),$$

where $\underline{R}_s$ is the s-th site of the lattice, and N_L is the number of lattice sites. The Wannier functions form a complete, orthonormal set over all bands and over all lattice sites, namely

$$\int a_m^*(\underline{r} - \underline{R}_j) a_n(\underline{r} - R_i) d\underline{r} = \delta_{mn} \delta_{ij}.$$

Moreover, each Wannier function $a_n(\underline{r} - \underline{R}_s)$ is localized around, associated with, the s-th site.

of bands is included in the expansion. As in all practical problems, however, through a judicious choice of localized, Wannier-like functions $w_n(\underline{r}, \underline{R}_s)$ (for example, a suitable linear combination of Wannier functions at the site $\underline{R}_s$), the summation over n may be reduced to a number equal to the number of valence electrons per atom, without great loss of accuracy. Thus, if different orbitals are used for different spins, a spin-orbital $u_i(q_j)$ may be adequately represented by the relation

$$u_i(q_j) = \sum_s \sum_n^v c_{in}(\underline{R}_s) w_n(q_j, \underline{R}_s), \tag{4}$$

where v is the number of valence electrons per atom, and $c_{in}(\underline{R}_s)$ is a constant.

Without loss of generality, suppose the crystal is that of a monovalent metal, v equals unity and the number N_L of lattice sites equals the number N of valence electrons. For this crystal, substitution of Eq. 4 into the determinental relation, Eq. 1, for the overall eigenfunction ψ_N yields

$$\psi_N = \frac{1}{(N!)^{1/2}} \begin{vmatrix} \sum_s c_1(\underline{R}_s) w(q_1, \underline{R}_s) & \cdots & \sum_s c_N(\underline{R}_s) w(q_1, \underline{R}_s) \\ \sum_s c_1(\underline{R}_s) w(q_2, \underline{R}_s) & \cdots & \sum_s c_N(\underline{R}_s) w(q_2, \underline{R}_s) \\ \cdot & \cdots & \cdot \\ \cdot & \cdots & \cdot \\ \cdot & \cdots & \cdot \\ \sum_s c_1(\underline{R}_s) w(q_N, R_s) & \cdots & \sum_s c_N(\underline{R}_s) w(q_N, \underline{R}_s) \end{vmatrix}, \tag{5}$$

where the subscript n equals unity has been omitted from the w's and the c's. Note that each column of the determinant in Eq. 5 is a linear combination of the N Wannier-like functions associated with the N sites of the crystal. It follows from the rules for the product of two determinants that Eq. 5 can be written in the form

$$\psi_N = \frac{1}{(N!)^{1/2}} \begin{vmatrix} w(q_1,\underline{R}_1) & \cdots & w(q_1,\underline{R}_N) \\ w(q_2,\underline{R}_1) & \cdots & w(q_2,\underline{R}_N) \\ \vdots & & \vdots \\ w(q_N,\underline{R}_1) & \cdots & w(q_N,\underline{R}_N) \end{vmatrix} \times \begin{vmatrix} c_1(\underline{R}_1) & c_2(\underline{R}_2) & \cdots & c_N(\underline{R}_1) \\ c_1(\underline{R}_2) & c_2(\underline{R}_2) & \cdots & c_N(\underline{R}_2) \\ \vdots & \vdots & & \vdots \\ c_1(\underline{R}_N) & c_2(\underline{R}_N) & \cdots & c_N(\underline{R}_N) \end{vmatrix} . \quad (6)$$

In the form of Eq. 6, the eigenfunction ψ_N for the whole crystal admits the localized spin-orbital interpretation which is sought. Indeed, note that each Wannier-like function $w(q,\underline{R}_s)$ is a spin-orbital associated with, localized around, lattice site $\underline{R}_s$ (the set of constants $C_i(\underline{R}_s)$, for $i = 1, 2, N$, is also associated with the same site $\underline{R}_s$). If the N electrons of the crystal are distributed among the N spin-orbitals $w(q,\underline{R}_s)$, an antisymmetric deter-minental function, Eq. 6, can be formed. This function is completely equivalent to that obtained from the delocalized orbitals. In other words, the ψ_N's constructed from either the localized or the delocalized spin-orbitals are identical.

It should be noted that the localized spin-orbitals $w(q,\underline{R}_s)$ are not energy eigenfunctions of the one-electron equations. Only ψ_N, Eq. 6, is an approximate eigenfunction of the Hamiltonian operator for the whole crystal. Never-theless, each localized spin-orbital can be assigned precise values for the ionization energy, electron affinity, and excitation energies of the electron in the spin-orbital, in a manner which is consistent with the usual definitions of these quantities. The values of the ionization energy, electron affinity, etc., of a localized spin-orbital are not equal to the corresponding values of the delocalized spin-orbitals. This point can be seen from the definition of the ionization energy given below.

Suppose that ψ_N, Eq. 6, represents the ground state of the crystal. The ionization energy of a spin-orbital localized around lattice site $\underline{R}_s$ is defined as the difference between the energy corresponding to an eigen-function ψ_{N-1} and that of the ground state. The eigenfunction ψ_{N-1} is given by Eq. 6 except that the s-th column and the s-th row of the first and the

second determinants are replaced by zeros, respectively, and $(N!)^{1/2}$ is replaced by $[(N-1)!]^{1/2}$. The Hamiltonian operator for ψ_{N-1} is that corresponding to N lattice sites and N-1 valence electrons. This defini-tion of the ionization energy assumes that removal of a localized spin-orbital from the system does not alter the functional dependence of the other N-1 localized spin-orbitals. Such an assumption is used in practically all approaches to the analysis of the electronic structure of solids (see, for example, Koopmans' theorem for the one-electron Hartree-Fock equations[11]).

The other energies of a localized spin-orbital can be defined in a manner analogous to that used for the ionization energy.

ELECTRONEGATIVITY AND CHEMICAL POTENTIAL

In this section, the work of the authors[4] on the identification of electronegativity with the negative of the chemical potential of an electron in an atom is summarized.[†]

In reference 4, an ensemble of identical, one-atom systems is con-sidered. Each atom is thought of as consisting of two components, electrons and ions. The systems are in thermodynamic equilibrium with a reservoir of electrons and ions at a small temperature T (degrees Kelvin). The components can flow back and forth between the systems and the reservoir. The energy eigenstates of the atoms are assumed to be derivable from the one-electron Hartree-Fock equations.[12] In other words, the electrons are viewed in an ideal substance.

According to the theory of statistics of ensembles,[13] the physical situation described above obeys the rules of grand canonical ensembles. Use of these rules yields the following important conclusions.

[†] Strictly speaking, the electronegativity has been identified with the electrochemical potential. For the reference level of energy selected in this paper, however, the values of the chemical and the electro-chemical potential are identical.

(a) Statistically, the energy E of an one-atom system can be expressed as a continuous function E(q) of a continuous variable q which represents a statistical measure of the charge in a valence spin-orbital. The range of the value of the charge q is from minus one electronic charge (-e), the orbital is doubly occupied, through zero, the orbital is occupied by one electron, to plus one electronic charge (+e), the orbital is ionized.

(b) The chemical potential μ_c of a valence electron is given by the relation

$$\mu_c = - (\partial E(q) / \partial q) \text{ at constant entropy.} \tag{7}$$

In the limit of very small temperatures, this potential is found to have the following exact values

$$\mu_c = - (I + A) / 2e \quad \text{for } q = 0 \quad \text{(neutral atom),}$$

$$\mu_c = \infty \quad \text{for } q = e \quad \text{(positive ion),}$$

and

$$\mu_c = - \infty \quad \text{for } q = -e \quad \text{(negative ion),}$$

where I and A are the first ionization energy and the electron affinity of the atom, respectively. The quantities I and A can also be referred to the valence electron spin-orbital.

(c) For fractional values q and for small T, μ_c is a function of both q and T.

(d) By virtue of (b) above, it is found that for small temperatures (in the limit of zero temperature) an excellent approximation for E(q) is given by the relation

$$E(q) = \frac{I + A}{2e} q + \frac{I - A}{2} [1 - (1 - \frac{q^2}{e^2})^{1/2}] \tag{8}$$

when the zero energy level is taken to be at the energy of the neutral atom (q equals zero). Note that this approximation yields exact values for E(q) and μ_c for q = -e, 0, e.

(e) The orbital electronegativity x(q) of a valence electron is defined as

$$x(q) = (\partial E(q) / \partial q) \text{ at constant entropy} =$$

$$= - \mu_c$$

This is the first time that a rigorous definition of x(q) is given.

(f) The value of the neutral orbital electronegativity x(0) obtained from Eq. 8 is identical to the value of electronegativity suggested by Mulliken[14]. It should be noted however, that Mulliken's value is considered to be approximate. Here, the thermodynamic analysis yields that, in the limit of small temperatures, x(0) has the exact value given by the relation

$$x(0) \equiv \frac{I + A}{2e} \tag{9}$$

(g) The definition of the orbital electronegativity given above can be easily extended to orbitals in systems other than atoms. Such an extension is discussed in the next section.

WORK FUNCTION AND ELECTRONEGATIVITY

Without loss of generality, consider a crystal of a monovalent metal, bounded by a uniform surface. Suppose the analysis of the electronic structure of this metal has been carried out with respect to a zero energy level taken at the points just outside the surface. Moreover, suppose that both the delocalized and the localized spin-orbitals have been established, in accordance with the procedure discussed in Section 2.

Thermodynamically, for a system of N-electrons, any set of N spin-orbitals which describes the system may be thought of as representing N degrees of freedom. When these N degrees of freedom are treated statistically, the following results can be obtained.

(a) Given the N delocalized spin-orbitals, one-electron spin-orbitals, the negative of the chemical potential of the surface, with respect to the points just outside the surface, equals the work function. This is the well-known thermodynamic definition of work function.[15,16]

(b) Given the N localized spin-orbitals, Wannier-like functions, suppose that all degrees of freedom are frozen except that corresponding to the spin-orbital localized around the surface site R_s. Under this condition, the surface spin-orbital can be treated statistically by the same procedure as that used for atoms in Section 3. In other words, this

orbital may be thought of as a surface atom. Thus, a chemical potential for the electron in the orbital can be defined. For example, in the limit of small temperatures, the value of the chemical potential of the localized spin-orbital equals

$$- (I_s + A_s)/2e,$$

where I_s and A_s are the ionization energy and the electron affinity of the orbital as defined in Section 2. This value equals the negative of the neutral orbital electronegativity of the spin-orbital, Eq. 9.

(c) From thermodynamic equilibrium considerations, it can be shown that the chemical potential of the localized spin-orbital as defined in (b) must be equal to the chemical potential of the surface, as defined in (a).[†]

(d) By virtue of (a), (b), and (c), it follows that the work function equals the neutral orbital electronegativity of a spin-orbital localized around a surface atom.

In conclusion: (a) the characterization of the electronic structure of metals by localized spin-orbitals is equivalent to the ordinary picture of electrons in metals; (b) electronegativity can be given a rigorous thermodynamic definition; and (c) the neutral orbital electronegativity of a surface spin-orbital, atom, equals the work function of the surface.

[†] The proof of this statement is analogous to that used in the study of chemical reactions with or without a catalyst.[17]

REFERENCES

(1)   STEINER, D.; GYFTOPOULOS, E. P., "An Equation for the Prediction of Bare Work Functions". Report 27th Annual Conf. Physical Electronics, MIT, Cambridge (1967) 160.

(2)   GYFTOPOULOS, E. P.; STEINER, D., "Orbital Electronegativity and Physical Properties of Bimetallic Adsorption Systems". Report 27th Annual Conf. Physical Electronics, MIT, Cambridge (1967) 169.

(3)   STEINER, D.; GYFTOPOULOS, E. P., "Orbital Electronegativity and Physical Properties of Metal-Gas Adsorption Systems". Report Thermionic Conversion Specialist Conf., San Francisco (1967) 145.

(4)   GYFTOPOULOS, E. P.; HATSOPOULOS, G. N., "Quantum Thermodynamic Definition of Electronegativity". To be published.

(5)   TOLMAN, R. C., "The Principles of Statistical Mechanics". Oxford University Press, New York (1938), pp. 312-324.

(6)   SLATER, J. C., "Quantum Theory of Molecules and Solids", Vol. 1, McGraw-Hill, New York (1963), p. 43.

(7)   SLATER, J. C., "Quantum Theory of Molecules and Solids", Vol. 3, McGraw-Hill, New York (1967), p. 265-271.

(8)   SLATER, J. C., "Quantum Theory of Molecules and Solids", Vol. 2, McGraw-Hill, New York (1965), p. 154-158.

(9)   KOSTER, G. F.; SLATER, J. C., "Wave Functions for Impurity Levels". Phys. Rev. 95 (1954) 1167.

(10)   Reference 6, Chapter 9.

(11)   Ibid., p. 96.

(12)   Ibid., Appendix 4.

(13)   HATSOPOULOS, G. N.; KEENAN, J. H., "Principles of General Thermodynamics". John Wiley, New York (1965), Chapter 48.

(14)   MULLIKEN, R. S., "A New Electroaffinity Scale". J. Chem. Phys. 2 (1934) 782.

(15)   Reference 13, pp. 557-558.

(16)   HERRING, C.; NICHOLS, M. H., "Thermionic Emission". Rev. Modern Phys. 21 (1949), p. 190.

(17)   Reference 13, pp. 329-330.