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Prediction of Fermi Energies and Photoelectric Thresholds Based on Electronegativity Concepts

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A simple formula involving the geometric mean of the electronegativities of the two components is proposed for the determination of the Fermi energies and hence the photoelectric thresholds of simple binary compounds, and is found to be surprisingly accurate for all presently available data. A theoretical basis for the use of the "postulate of the geometric mean" is also given.

The concept of *atomic* electronegativity has been extremely useful since its inception,[1] in systematizing chemical trends in thermochemical data (bond-formation energies) and, to a lesser degree, trends in the spectroscopic behavior of atoms.[2] More recently, it has been noted that an ionicity scale (and hence an electronegativity) for many binary *compounds* can be defined based on their spectroscopically measured electronic polarizabilities and that other material properties can be correlated with position on this scale.[3] This paper will demonstrate that a very simple relationship based on *atomic* electronegativities and suggested by the original ideas of Pauling and Mulliken is surprisingly accurate in predicting, relative to the vacuum level, the intrinsic Fermi energies ($E_F{}^i$) of a very wide variety of simple binary compounds. For comparison with experimental photoelectric threshold energies (Φ_{exp}), one half of the optical energy gap (E_g) is added to $E_F{}^i$. Since most of the accurate values of Φ_{exp} are quite recent, tests of such relationships would not have been as definitive in the past. Although we use electronegativities derived from bond-formation energies to derive spectroscopic information on compounds, it is equally possible to use such spectroscopic information (i.e., Φ_{exp} and E_g) to predict bond-formation energies accurately.

Mulliken noted[2] that for the "one-electron" Group-I and Group-VII elements the electronegativity, x, should be proportional[4] to the average of the first ionization potential, Φ, and the electron affinity, χ:

$$M_A \equiv (\Phi_A + \chi_A)/2 = 2.86 x_A \text{ (in eV)}, \tag{1}$$

where M_A will be called the Mulliken potential. Mulliken also recognized that, in the compound AB, electron redistribution will establish $M_A = M_B$ to produce thermodynamic equilibrium among the excited electron states, χ, just as the Fermi energy is used in semiconductor-junction problems. Equation (1) was used by Pauling to help establish the origin for his electronegativity

TABLE I. Comparison of experimental[a] and calculated photoemission thresholds.

	E_g (exp)	E_F^i (Eq.3)	Φ_{calc} (Eq.4)	$\frac{\Phi_{calc}}{\Phi_{exp}}$
		IV		
Si	1.10	5.15	5.70	1.025
Ge	0.70	5.15	5.50	1.025
		III-V		
InP	1.30	5.40	6.05	1.02
GaAs	1.40	5.11	5.81	1.01
InAs	0.38	5.26	5.45	.98
AlSb	1.64	4.84	5.66	.975
GaSb	0.70	4.98	5.33	1.005
InSb	0.18	5.15	5.24	.975
		II-VI		
ZnO	3.26	6.77	8.40	1.05
ZnS	3.62	5.71	7.52	.99
CdS	2.46	5.90	7.13	.98
HgS	0	6.25	6.25	1.04
ZnSe	2.74	5.60	6.97	1.015
CdSe	1.68	5.78	6.62	.99
HgSe	0	6.12	6.12	1.09
ZnTe	2.22	5.25	6.36	1.06
CdTe	1.50	5.40	6.15	1.03
HgTe	0	5.73	5.73	.96
		I-VII		
KF	11.0	5.12	10.60	1.015
NaCl	8.7	4.70	9.05	1.06
KCl	8.7	4.43	8.80	1.01
CsCl	∿8.5	4.15	8.40	1.09
KBr	7.8	4.29	8.20	.98
CsBr	7.9	4.00	7.95	1.09
LiI	5.8	4.52	7.40	1.01
NaI	5.7	4.29	7.15	.985
KI	6.0	4.05	7.05	.98
RbI	6.0	4.05	7.05	.99
CsI	6.2	3.78	6.90	1.07

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scale. The basis for this scale is the relationship

$$D_{AB}=(D_{AA}D_{BB})^{1/2}+30(x_A-x_B)^2 \quad \text{(in kcal/mol)}, \tag{2}$$

where D_{AB} is the bond energy between atoms A and B, etc. The first term[5] embodies the "postulate of the geometric mean."

If an analogy is drawn between the bond energies for like atoms, D_{AA}, and the atomic electronic energies as represented by M_A, then to zeroth order the relation $M(AB)=(M_AM_B)^{1/2}$ *might* be obeyed. Since excitation of an electron from atom A to atom B (or vice versa) can correspond to conduction-band electrons in the solid (as contrasted to the necessarily excitonlike internal excitations within A or B), it also appears that $M(AB)$ should merge with $E_F{}^i(AB)$ in the solid and hence

$$E_F{}^i(AB)\equiv(\Phi_{AB}+\chi_{AB})/2=2.86(x_Ax_B)^{1/2}. \tag{3}$$

The related expression for the photoelectric threshold is

$$\Phi_{calc}{}^{AB}=2.86(x_Ax_B)^{1/2}+E_g/2. \tag{4}$$

The above is, of course, simply a plausibility argument which must be checked against experimental results.

Values of E_g, $E_F{}^i$, Φ_{calc}, and the comparison to Φ_{exp} are given in Table I. An overview is presented in the histogram of Fig. 1. The obvious good agreement is obtained without adjustment of the single proportionality constant, 2.86, from that derived from information on *atomic* states. Another feature is that contamination (or decomposition) of the surface would usually tend to lower Φ_{exp}, and hence results for such surfaces would lie on the right-hand side of the histogram. The error in Φ_{exp} for good surfaces probably lies between ±0.1 and ±0.3 eV (about ±4%). Values of $x_{A,B}$ are only accurate to within about ±0.05 units and thus errors in Φ_{calc} should be limited to within ±3%. Thus, if Eq. (4) is accurate, most of the values of Φ_{calc}/Φ_{exp} should lie between 0.95 and 1.05, which is very much the case. Thus Eq. (4) works well for a wide variety of simple binary compounds with $E_F{}^i$ ranging from 3.8 eV (CsI) to 6.8 eV (ZnO), Φ from 5.2 eV (InSb) to 10.6 eV (KF), and E_g from 0 eV (HgSe) to 11.0 eV (KF).[6]

The values of Φ_{exp} used in Table I correspond to photon energies at which the photoelectric yield, Y, becomes "substantial." Where avail-

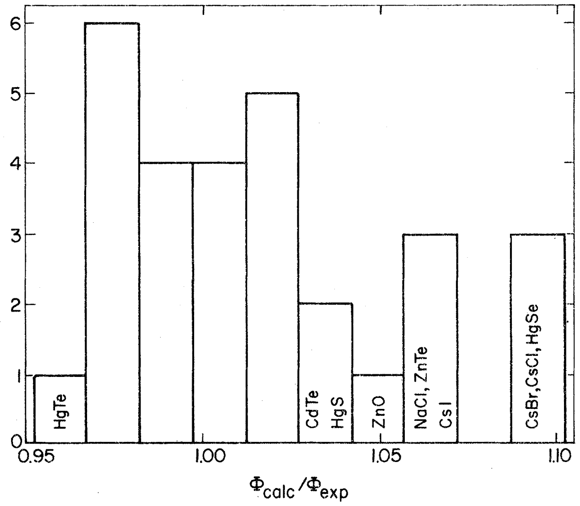

FIG. 1. Histogram of the frequency of occurrence of values of Φ_{calc}/Φ_{exp}.

able, this energy is an average using three criteria: that energy at which $Y=10^{-4}$, the linearly extrapolated energy-distribution-curve (EDC) width (which neglects the tails), and values of $h\nu_{d1}$ at which Y versus $\hbar\omega$ first departs from linearity. A different definition, Φ_{exp}, based on the low-yield emission tails is possible for the two group-IV, the six III-V, and seven of the II-VI materials. The criteria used for Φ_{exp}' are the zero intercepts of the $Y^{1/3}$ (or sometimes $Y^{1/2}$) versus $\hbar\omega$ curves and the EDC width including tails. The histogram for Φ_{calc}/Φ_{exp}' (not shown) is very flat and non-Gaussian with little structure and it extends from 1.00 to 1.14. Thus the agreement is not as good as for Φ_{exp}. However, the theoretical justification behind such $Y^{1/3}$ (or $Y^{1/2}$) extrapolations is not well established[7] and the choice of the exponent tends to be empirically determined. Independent of what the nature of these emission tails is eventually determined to be, Eq. (4) is surprisingly accurate in predicting where "substantial" photoemission occurs and less accurate for the low-yield "tail intercepts."

Values of Φ_{calc}/Φ_{exp} lie outside of the expected range for only six of the 29 compounds. Three are cesium halides and Φ_{exp} could easily be decreased by some excess Cs on the surface (Cs is known to lower Φ drastically for a variety of materials). Only one early measurement is available for NaCl. For HgSe also only one measurement[8] is available. However, for the series CdS, CdSe, and CdTe, the d-electron core-to-vacuum spacing is found[8] to be constant within ±0.13 eV, whereas for HgS and HgTe a variation of ±0.4 eV is reported with the HgTe core lying deepest and for ZnSe and ZnTe the variation is ±0.28 eV with ZnSe deepest (i.e., in the opposite direction). The use of values of Φ_{calc} from Eq. (4) rather than Φ_{exp} (Ref. 8) results in a constant d-core depth for both the latter series, just as reported for the Cd series (for which $\Phi_{calc}=\Phi_{exp}$).[9] Similarly Φ_{exp} for HgS (and ZnTe) may also be too low. Thus, Eq. (4) probably is considerably more accurate than Fig. 1 indicates.

The rationale for the *ad hoc* use of the postulate of the geometric mean in Eq. (3) becomes evident from a simple charge-transfer model based on the Mulliken potentials, $M_{A,B}$. The two atomic levels can be represented by quasihydrogenic formulas of the form $E=RZ_{eff}^2/n^2$:

$$\Phi_A=(R/n^2)[1+\alpha_A'+\delta_A'+q(1+2\delta_A')]^2, \qquad (5)$$

$$\chi_A=(R/n^2)[\alpha_A'-\delta_A'+q(1+2\delta_A')]^2. \qquad (6)$$

The unit core charge for Φ_A is augmented by the core penetration factor α_A', and δ_A' allows this factor to be nonidentical for the atom and the negative ion. The term in q allows for charge flow from atom A to atom B in the compound AB. Also, the condition $\Phi_A(q=0)=\chi_A(q=1)$ is used. With the substitution of $\alpha_A\equiv\alpha_A'+\frac{1}{2}$ and $\delta_A\equiv\delta_A'+\frac{1}{2}$, it is then found that

$$M_{A,B}=(R/n^2)[(\alpha_{A,B}\pm 2q\delta_{A,B})^2+\delta_{A,B}^2], \qquad (7)$$

where the negative sign corresponds to atom B.

Letting $M_A=M_B$ in the compound AB, solving for q, and substituting q back into Eq. (7) and since $E_F^i(AB)=M(AB)$, we obtain

$$E_F^i(AB)/M_A^0=n(1+K)/(1+Kn) + (1+f_A^2)(n-1)^2/8(n+1), \qquad (8)$$

where $n=M_B^0/M_A^0=x_B/x_A$, $f_A=\delta_A/\alpha_A$, $K=f_B(1+f_A^2)/f_A(1+f_B^2)$, and an accurate approximation has been made in the small second term.

If it is assumed that $f_A=f_B=1$, Eq. (8) reduces to

$$E_F^i(AB)/M_A^0=(n^2+6n+1)/4(1+n). \qquad (9)$$

For $1\leq n\leq 4$, Eq. (9) is an excellent approximation to the geometric mean, $\sqrt{n}$. For $f_{A,B}<1$, compensating changes occur in the first and second terms of Eq. (8). For a certain functional relationship between f_A and f_B with n as a parameter, Eq. (9) is *exactly* maintained. Calculation of $f_{A,B}$ from experimental data for Φ and χ for the "one-electron" Group-I and Group-VII elements yields values close to those given by this relationship.

Alternatively, these experimental values of $f_{A,B}$ can be used directly in Eq. (8) with the results obtained lying within 4% of $\sqrt{n}$ in all cases. Even for elements from other groups (for which $M_{A,B}$ and $f_{A,B}$ from spectroscopic data may need some correction[2]), the uncorrected values of $f_{A,B}$ lie approximately in this same range in most cases.

Among various observations that can be made based on the above are the following: (1) For an undoped stoichiometric compound, $E_F{}^i$ is determined solely by the electronegativities of the constituent elements and hence is not structure or coordination sensitive; E_g clearly is so sensitive. (2) $E_F{}^i$ can be accurately predicted without *any* recourse to solid-state data. The present approach differs in this respect from the dielectric model of Phillips, which has been applied by Van Vechten[10] to photoemission thresholds. For the series C, Si, Ge, and Sn, this treatment requires data on Φ for two of these compounds to predict the other two. A value of $\Phi' = 4.09$ for Sn is thus obtained, whereas our treatment predicts that $\Phi = 5.15$. Allowing for the difference between Φ and Φ', the discrepancy is still almost 1 eV. Data for Sn are not available, but data on InSb (which brackets Sn) are. The dielectric-model result for Φ' is 4.61 compared to 5.07 measured, whereas our result for Φ is 5.24 compared to 5.37 measured. This indicates that our results are to be preferred over those of the dielectric model, at least for Sn and InSb. (3) Surface-orientation effects would be expected to influence Φ; since they are not included and Eq. (4) is apparently accurate to ± 5%, such effects on Φ (but not necessarily Φ') would also seem to be less than 5% for these binary compounds. (4) It is seen that charge-transfer effects are strongly involved in the "postulate of the geometric mean" for $M(AB)$ and hence it is likely that both terms of Eq. (2) also depend markedly on electronegativity differences. (5) It is now possible to estimate many unknown emission thresholds and compare them to new results or to identify existing data which may be suspect (e.g., HgSe and ZnTe). (6) In problems involving the flow of charges between layers of different materials, it should now be easier to separate bulk effects from interface effects; such problems are becoming more important both technologically and scientifically. (7) The close identity of spectroscopically defined and thermochemically defined atomic electronegativities is even more firmly established.

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[9] This suggests that, for a given series, it may be more valid experimentally to index the top of the valence band relative to the *d*-core level rather than to the trailing edge of the EDC curves. Measurements on ZnS and ZnO (J. L. Freeouf, D. E. Eastman, M. Erbudak, and W. D. Grobman, to be published) further support this possibility. Their valence-band-to-*d* separations are < 9.0 eV and 7.65 eV, respectively, which when added to Φ_{calc} become < 16.5 eV and 16.05 eV, respectively. The values for ZnTe and ZnSe are 16.0 and 16.2 eV.

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