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Negative Electron Affinities of Nonmetallic Elements

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A method is developed for calculating second and third electron affinities of atoms. The method is based on the use of Slater orbitals, but orbital exponents are found empirically for each element by using known values of I and A for that element. A_2 is found for O, S, and Se and A_2 and A_3 for N, P, and As. The results are tested by applying the Born–Mayer ionic model for bonding to a number of MX solids. As expected, MX solids with CN = 6 give good results for cohesive energies, using the ionic model and the new values of A_2 and A_3. Solids with CN = 4 give poor results, showing much greater covalent bonding.

Introduction

The first electron affinities, A_1, are now known for most of the elements.[1] However, all multiply charged monatomic anions are unstable in the gas phase. Hence values of the second and third electron affinities, A_2 and A_3, are not available by direct experiment. Still there are good reasons to believe that anions such as O^{2-} or N^{3-} may exist in the solid state, in so-called ionic solids.

The best experimental approach to higher electron affinities is to assume that the anion does exist in the solid and to apply the Born–Mayer ionic model to calculate the cohesive energy of the solid.[2]

$$MX(s) = M(g) + X(g) \quad \Delta E_0^\circ \tag{1}$$

Comparison with experimental values of ΔE_0° then enables a calculation to be made of A_2 or $A_2 + A_3$.

The best results of this kind are for the alkaline-earth-metal oxides, MgO to BaO. A careful analysis of these solids leads to an A_2 for oxygen of −183 kcal/mol.[3] Of course, if the solid is not as ionic as assumed, this method will lead to poor results.

The Born–Mayer model uses point charges, but this restriction can be removed. Cohen and Gordon used a model with the electron density for each ion obtained from single-center atomic orbitals.[4] Their estimate of A_2 for oxygen was −169 ± 7 kcal/mol.

Ab initio quantum-mechanical calculations of negative electron affinities face a fundamental problem. The lowest energy of the system will place the added electron at infinity, and give an A_2 or A_3 of zero. Nevertheless, the Hartree–Fock energies of O^{2-} and other doubly negative ions have been calculated.[5] This is possible by applying the constraint that all of the valence shell p orbitals have the same radial function. Combining the HF energy of O^{2-} with that of the oxygen atom[6] gives $A_1 + A_2 = -189.5$ kcal, with the experimental value of A_1 being 33.7 kcal.[1] Since this calculation does not include the very large difference in correlation energies between O and O^{2-}, all we can say is that A_2 is less negative than −223 kcal.

Even for the most favorable case of oxygen, the best value to use is not clear. For the other nonmetallic elements, the situation is even worse. But it seems to be imperative that we have reliable values of A_2 (and A_3) for these elements, if we wish to understand chemical bonding in the solid state. Since purely theoretical, or purely experimental, results are not available at this time, the possibility of a semiempirical method should be considered.

For all the important elements, we have reliable values of A_1 and of $I_1, I_2, I_3, ...,$ the successive ionization potentials. The purpose of this paper is to find values of A_2 and A_3 by a suitable extrapolation from the known data. We will restrict ourselves to the elements O, N, S, P, Se, and As, the most likely candidates to form multiply charged ions. They also have the great advantage that only electrons with the same values of n and l, for each atom, need to be considered, if we assume that the added electrons simply fill up the subshell. All the electrons in the same subshell will have the same radial distribution.

The usual way of treating successive values of I for such cases is to write a quadratic equation

$$E = E_0 + aN + bN^2 \tag{2}$$

where N is the number of similar electrons.[7] Unfortunately, this equation does not work well, if we attempt to continue it to negative ions. For example, it predicts A_1 for fluorine to be −3.3 kcal, instead of the correct +78.4 kcal.

The reason for the failure is easy to find. The parameter a represents a core integral, and b, the valence shell interelectronic repulsion integrals.[7] But these integrals are functions of the orbital exponent ζ that occurs in the radial part of the wave function. And ζ is not constant, but decreases as N increases.

This suggests a method based upon the use of Slater orbitals,[8] which have the property of changing ζ as N changes. The Slater orbitals used in this work are of the form

$$\chi = C^{1/2} r^{n-1} e^{-\zeta r} \cos\theta \tag{3}$$

where $n = 2, 3, 4$. The orbital exponent $\zeta = (Z - s)/n^*$, where s is the screening constant and depends on the number of electrons. The quantum number n^* is equal to n, except for $n = 4$, where $n^* = 3.7$. Z is the nuclear charge, and C is a normalization constant.

Slater's rules enable s to be calculated at once, and hence ζ. The ionization potential for any orbital in any atom in any stage of ionization can then be readily found.[8] The answer will be only approximate and is not nearly good enough for our purposes. Instead, a method will be described next that gives highly accurate results, for cases where the answer is known. The method selects a particular atom and uses its known values of I and A to calculate values that are adjacant, and perhaps unknown.

Details of the Calculation

The master equation is[9]

$$I = -\zeta^2/2 + \zeta G \tag{4}$$

where $\zeta^2/2$ is the kinetic energy in atomic units and $-\zeta G$ is the total potential energy of an electron in a particular orbital. Thus (4) gives the orbital energy, with sign changed, which is equal to I by Koopman's theorem. This theorem is in error by the reorganization energy, but this is compensated for by using experimental values of I to calibrate (4). The same equation also applies for electron affinities, by simply replacing I by A.

The general procedure is to start with the neutral atom and to calculate its orbital exponent, ζ°, by Slater's rules. Then I_1 is used in eq 4 to calculate G°. Next proceed to A_1 and use (4) to calculate ζ for the anion. First, however, G must be recalculated, since it differs from G° by the potential energy of the second electron interacting with the first, if the spins are the same. If the spins are opposite, there will also be changes in exchange energy.

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The change $\zeta^\circ - \zeta = \Delta\zeta$, is a function of $G^\circ - G$, since the change in shielding responsible for $\Delta\zeta$ is due to the difference in interelectronic repulsion.

The next step is to use (4) to calculate A_2, after correcting G again as before. The change in G fixes the value of ζ for the doubly charged anion, from the previous result for $\Delta\zeta$. Thus everything in eq 4 is known, except the unknown A_2. The value of A_3 can also be found by repeating the procedure for A_2.

The changes in G are readily calculated from the cases of interest, since they are simply Coulomb and exchange integrals for two electrons in two 2p, 3p, or 4p orbitals. The formulas for calculating these integrals for Slater type orbitals are found in the literature.[10]

An example will be given in more detail. Let us find A_2 for oxygen. For O, ζ° is found to be 2.275 by Slater's rules. I_1 for O is 13.62 eV, or 0.501 in atomic units of energy.

$$I_1 = 0.501 = -2.588 + 2.275G^\circ \qquad (5)$$

$$A_1 = 0.054 = -\zeta^2/2 + \zeta(G' - 0.3283) \qquad (6)$$

After one solves for $G^\circ = 1.3578$, a small correction, −0.0024, is made to get G'. The reason for this is described in the Appendix. The quantity 0.3283 in (6) comes from $J_{xy} - K_{xy} = 0.3283\zeta$ where J_{xy} and K_{xy} are the Coulomb and exchange integrals for two electrons in different 2p orbitals, and with the same spin.

Solving the quadratic equation (6), we find $\zeta = 2.000$ for O^-, so that $\Delta\zeta = -0.275$. Slater's rules would give $\Delta\zeta = 0.175$. The addition of a second electron to form O^{2-} also produces a change in G equal to $J_{xy} - K_{xy}$. Therefore $\Delta\zeta$ is the same and ζ for O^{2-} is 1.725. We can now find A_2.

$$A_2 = -1.4878 + 1.725(1.0267 - 0.3283) = -0.283 \text{ au} = -178 \text{ kcal} \qquad (7)$$

As a check on the transferability of $\Delta\zeta = -0.275$, we calculate A_1 for fluorine. As before, G° is found from I_1 for F. $\zeta^\circ = 2.60$ for F, and $\zeta = 2.325$ for F^-. This gives $A_1 = 0.123$ au, or 77.2 kcal, compared to the experimental value of 78.4 kcal. Using Slater's rules would give $\Delta\zeta = -0.175$, and $A_1 = 4.5$ kcal.

An alternative application of eq 4 is to use I_1 and I_2 to predict a value of I_3. This was done for Ne, Ar, and Kr, as a test of the method. For Ne, the calculated value of I_3 is 63.48 eV, and the experimental value is 63.47 eV. For Ar, the calculated value is 40.81 eV, and the experimental value is 40.82 eV. The values of $\Delta\zeta$ were found to be 0.240 for Ne and 0.104 for Ar. These may be compared to a $\Delta\zeta$ of 0.175 for Ne and 0.117 for Ar, found by Slater's rules.

For krypton poor results were found. I_3 was calculated to be 32.89 eV, compared to 36.96 eV actual. Also $\Delta\zeta$ was found to be only 0.030, compared to 0.095 from Slater's rules. It may be recalled that for $n > 3$, Slater's orbitals are not nearly as good as for the lighter elements. For example, effective quantum numbers, n^*, are no longer integral. However, in the case of Kr, it was found that no other value of n^* gave better results than $n^* = 3.7$, using eq 4.

The problem really arises because only 1s, 2p, 3d, and 4f Slater orbitals are proper orbitals, orthogonal to all other orbitals of the same or lower n. They are also hydrogenic orbitals, so that $\zeta^2/2$ is the mean kinetic energy, as in eq 4. The 3p and 4p Slater orbitals are only good approximations far from the nucleus. Closer in they must be supplemented by other orbitals, to make them orthogonal to the 2p orbital and to each other.

They also are not hydrogenic and their nominal kinetic energies are only $0.2333\zeta^2$ and $0.1429\zeta^2$, respectively, Slater assumed that the supplemental orbitals, with high orbital exponents, would raise the kinetic energies to $0.500\zeta^2$. This value is required by the virial theorem to find ionization potentials by the Slater method.

Apparently this occurs for a 3p orbital, but not a 4p. With krypton used as a test, the coefficient of ζ^2 in (4) was varied from 0.500. It was found that a kinetic energy of $0.200\zeta^2$ gave the best results. That is, I_3 was calculated to be 36.70 eV, closer to 36.96 than any other choice for the coefficient.

Accordingly, for Se and As all results were calculated from the modified equation

$$I = -0.200\zeta^2 + \zeta G \qquad (8)$$

While the theoretical basis for (8) is greatly weakened, it can still serve as an empirical equation for extrapolating from known values to unknown values of I and A. Support for this statement comes from a calculation of A_1 for Cl, using (4), and Br, using (8). The values found are $A_1 = 83.5$ kcal and experimental $A_1 = 83.5$ for Cl and $A_1 = 77.7$ kcal and experimental $A_1 = 77.5$ for Br.

Table I. Electron Affinities of Nonmetallic Elements

	O	S	Se
A_1[a]	33.6	48.0	46.6
A_2[b]	−178	−109	−98
	N	P	As
A_1[a]	1.7	17.1	18
A_2[b]	−161	−112	−104
A_3[b]	−256	−212	−192

[a] Experimental, kcal/mol. [b] This work, kcal/mol.

Results and Discussion

Table I summarizes the results found for the higher electron affinities of O, N, S, P, Se and As. The known values of A_1 are also included. A_2 and A_3 are all negative numbers, as expected. The relative values seem to be very reasonable. The result for oxygen is in the middle of the range of other estimates.

The Hartree–Fock calculations allow us to calculate $A_1 + A_2$ for several of the elements.[5,6] These may be compared to the sum found in the present work.

$$X + 2e^- = X^{2-} \quad A_1 + A_2$$

	$A_1 + A_2$, kcal			
	O	N	S	P
Hartree–Fock	−189	−212	−86	−116
present work	−144	−160	−61	−95

Since the HF numbers will become more positive when the correlation energy correction is made, the overall agreement seems to be good.

The best test of the new electron affinities, of course, is to use them in the calculation of cohesive energies of suitable solids. This will be done next for some binary MX compounds. The Born–Mayer equation will be used.[2]

$$U_0 = -\frac{AZ^2}{R_0}\left(1 - \frac{\rho}{R_0}\right) \qquad (9)$$

$$\frac{v_0}{\beta} = \frac{AZ^2}{9R_0}\left(\frac{R_0}{\rho} - 2\right) \qquad (10)$$

A is the Madelung constant, Z is the magnitude of the ionic charge, R_0 is the equilibrium separation in the solid, and ρ is the constant in the repulsion term $Be^{-R/\rho}$.

To find ρ we need the molar volume, v_0, and the compressibility, β. Reliable values of β are available only for a limited number of solids.[12] Regularities in v_0/β for related solids allow estimates to be made in other cases.[13] But when Z is 2 or 3, small errors in these estimates can lead to large errors in the equilibrium potential energy, U_0.

Referring back to eq 1 for the cohesive energy, the working equation is

$$\Delta E_0 = -\sum_{2,3} I_i + \sum_{2,3} A_i - U_0 \simeq \Delta H_{298}{}^\circ \qquad (11)$$

The small difference between $\Delta E_0{}^\circ$ and ΔH° at 298 K is ignored. Also, U_0 is not corrected for van der Waals energies.[3]

Table II contains a sampling of calculated values of $\Delta E_0{}^\circ$ and the experimental values of ΔH°. The strategy is to pick one example of MX with the rock salt structure, coordination number 6, and one with the sphalerite or wurtzite structure, coordination number 4. The evidence is very strong that the former are highly ionic and the latter are more covalent.[14] Therefore, the ionic

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Table II. Comparison of Experimental and Theoretical Values for the Cohesive Energies of MX Solids

MX	CN	$\Delta H^{\circ a}$	$\Delta E_0^{\circ b}$	MX	CN	$\Delta H^{\circ a}$	ΔE_0^{b}
CaO	6	254	251	LaN	6	289	285
ZnO	4	174	130	GaN	4	206	155
CaS	6	222	193	CeP	6	~260[c]	242
ZnS	4	147	86	InP	4	155	-27
CaSe	6	185	172	CeAs	6	247	224
ZnSe	4	125	57	GaAs	4	156	-65

[a] Experimental values, kcal/mol. Data taken from ref 11. [b] Theoretical values from ionic model, eq 11. Values for R_0 from: Wyckoff, W. G. *Crystal Structures*; Interscience: New York, 1970; Vol. 1, Chapter 3. [c] Interpolated from data for CeN, ΔH° = 292 kcal/mol, and CeAs, ΔH° = 247 kcal/mol.

model should work well for CN = 6, and should give values of ΔE_0 that are too small for CN = 4.

The results in Table II are in accord with expectations, assuming that the values of A_2 and A_3 used are reasonably good. The CN = 6, or ionic, compounds give calculated values of ΔE_0° that are in good agreement with experimental ΔH°. Except for LaN and CaO, the difference of 10–20% is what might be expected from covalent bonding. Apparently the first two are highly ionic.

The MX compounds with CN = 4 all give theoretical values that are much too small, requiring a great deal of covalent bonding. Even ZnO requires covalent bonding amount to 25% of the total cohesive energy. The negative values found for InP and GaAs show that the ionic model is completely inappropriate.

In the case of the compounds in Table II, and in many others, the choice of CN = 4 or 6 comes entirely from the sum of the ionization potentials in eq 11. For example, $I_1 + I_2 + I_3 = 1215$ kcal for indium, but only 842 kcal for cerium. Thus it is too costly to form In^{3+}.

The method used to obtain A_2 and A_3 shows that they are properties of gas-phase ions. But the results in Table II seem to show that there is little effect on going to the solid state. While this result is quite surprising, it is the same one found earlier when the ionic model was applied to the alkali-metal halides.

We may also infer that the Slater orbitals formed by changing the orbital exponents in the wave functions in (3) are good representations of the outermost parts of the ionic wave functions in the solid state. It is instructive to calculate the radius of maximum radial charge density, $R_{max} = n/\zeta$, for the anions we have been discussing.

Table III shows the values of R_{max}, R_{ion}, and ζ for the common monatomic anions. The values of ζ are those found in this work, and n = 2, 3, or 4. The R_{max} numbers are always much less than the conventional ionic radius, R_{ion} (As^{3-} is something of an exception). The reason for this has been given by Slater.[16] Since the overlap of filled shells can only lead to repulsion, it is advantageous to keep the regions of maximum electron density well separated. For example, in CaO the value of R_0 is 2.41 Å, but the sum of R_{max} for the anion and for the cation[16] is only 1.15 Å.

Table III. Properties of the Common Monatomic Anions Based on Slater Orbitals

	$R_{max}{}^a$	$R_{ion}{}^b$	ζ^c
F^-	0.46	1.36	2.323
Cl^-	0.84	1.81	1.890
Br^-	1.13	1.95	1.869
O^{2-}	0.61	1.40	1.724
S^{2-}	1.03	1.84	1.530
Se^{2-}	1.40	1.98	1.507
N^{3-}	0.98	1.71	1.079
P^{3-}	1.41	2.12	1.137
As^{3-}	1.89	2.22	1.119

[a] Calculated radius of maximum electron density for the outer orbital, in Å. [b] Pauling ionic radii, in Å. [c] Values found in this work.

Concluding Remarks

In summary, it appears that the numbers shown in Table I are very good approximations to the energy changes due to adding more than one electron to an atom. However, no claim is made that they have been rigorously derived and are highly accurate. In spite of the greater electronegativity of oxygen, it is much more difficult to form O^{2-} than S^{2-} or Se^{2-}. This results from the smaller value of R_{max} for O^{2-}, which means that interelectronic repulsions are much greater. Similar remarks apply to N^{3-} compared to P^{3-} and As^{3-}. In other language, O and N have a small charge capacity because of their sizes.[17] Also O and N are much harder than the other members of their families.[18]

Appendix

While it is convenient to write the potential energy as $-\zeta G$ in eq 4, it is not strictly true in the case of the interaction of two electrons in orbitals with different values of ζ. For example, in the oxygen atom, $\zeta = 2.275$ for the 2p electrons and $\zeta' = 7.70$ for the 1s electron, using Slater's rules. The Coulomb integral between these two orbitals is readily found to be[10]

$$J = \frac{\zeta}{2}\left[1 - \frac{\zeta}{\zeta' + \zeta} - \frac{2\zeta'\zeta^4}{(\zeta' + \zeta)^5}\right] \tag{12}$$

This gives $J = 0.4964\zeta$, for the starting value of ζ. If the orbital exponent is now decreased to $\zeta = 2.000$, we calculate $J = 0.4976\zeta$, the correct value. We would incorrectly assume J is still equal to 0.4964ζ.

The error of -0.0012ζ is multiplied by 2, since there are two 1s electrons. For sulfur the error due to the 1s electron can be ignored, but not the 2s and 2p shell error. The error per electron is only half as great per electron, but there are eight electrons in n = 2.

For selenium and arsenic, no attempt was made to estimate the error, because of the uncertainties in the outermost orbitals. Small corrections were made in all other cases.

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(15) Reliable compressibility data were used for the results in Table II, except for ionic CaSe, LaN, CeP and CeAs, where no data were available and models had to be used.

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