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Connection between energy relations of solids and molecules

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The universal energy relation, discovered for metallic and covalent solids as well as nuclear matter, is tested for diatomic molecules. We find that it applies well to covalent diatomic bonds, but that ionic diatomic bonds are in a distinct class. A simple extension of the universal binding energy relation that includes the effects of ionicity ensues. It yields accurate predictions of spectroscopic data for both ionic and covalent bonds in 150 molecules. The form of the covalent part is given by the universal relation, suggesting an intimate relationship between the energetics of solids and diatomic molecules.

A universal relationship between total energy and distance between atoms in solids has been discovered for metallic and covalent bonds in adhesion,[1] chemisorption,[2] and cohesion.[3] It has been reported to extend to covalent diatomic molecules[4] and even nuclear matter.[5] How the energetics of diatomic molecules could be of the same form as that of bulk solids is one of the intriguing questions arising from this discovery. The electron density seen by each atom from all other atoms has recently been shown[6] to provide a link between energy relationships in molecular and solid-state configurations.

Graves and Parr[7] (GP) carried out extensive tests of the universal relationship for diatomics. They evaluated scaling properties of $[d^3E(R)/dR^3]_{R_e}$ and $[d^4E(R)/dR^4]_{R_e}$ using spectroscopic data on 150 molecules. Here $E(R)$ is the total energy as a function of interatomic spacing R, and R_e is the equilibrium separation.[8] Their conclusion was that the universal relationship was at best only moderately well satisfied for the 150 diatomics.

Does this mean that the universal energy relation applies only to solids and nuclear matter and fails for the molecular configuration? In this paper we attempt to answer that question. Our findings suggest that the apparent limitation does not involve the molecular configuration. Rather, we find that it is due to the fact that as a result of charge transfer ionic bonds form a universality class that is distinct from that of covalent bonds. A simple energy relationship ensues for the partially ionic class which includes the universal relationship and the charge transfer. Thus a simple form is consistent with spectroscopic data for the 150 diatomics. The covalent part is the universal relation for metallic and covalent solids, suggesting that those solids and diatomic molecules have features common to their energy relations.

The universal energy relation is of the following simple form:

$$E=D_eE^*(a^*)\ , \tag{1}$$

where

$$a^*=(R-R_e)/l\ . \tag{2}$$

Here D_e is the molecular dissociation energy, $E^*(a^*)$ is a scaled energy relation, and l is a scaling length defined as $l=\{D_e/[d^2E(R)/dR^2]_{R_e}\}^{1/2}$ so that Eq. (1) gives the correct value of $[d^2E(R)/dR^2]_{R_e}$ with $[d^2E^*(a^*)/da^{*2}]_0\equiv 1$ for convenience. Eqs. (1) and (2) are considered universal for a class of matter when a *single* $E^*(a^*)$ accurately describes the energetics of the entire class. Following GP,[7] we define

$$k_e\equiv[d^2E(R)/dR^2]_{R_e}\ , \tag{3}$$

$$l_e\equiv[d^3E(R)/dR^3]_{R_e}\ , \tag{4}$$

$$m_e\equiv[d^4E(R)/dR^4]_{R_e}\ , \tag{5}$$

and[8]

$$\Delta \equiv k_e R_e^2 / 2D_e \ . \tag{6}$$

It follows from Eqs. (1)–(6) that

$$a_1^2/\Delta \equiv (\tfrac{2}{9}) D_e l_e^2 / k_e^3 = (\tfrac{2}{9})[d^3E^*(a^*)/da^{*3}]_0^2 \tag{7}$$

and

$$a_2/\Delta \equiv (\tfrac{1}{6}) D_e m_e / k_e^2 = (\tfrac{1}{6})[d^4E^*(a^*)/da^{*4}]_0 \ . \tag{8}$$

That is a_1^2/Δ and a_2/Δ are equal to universal constants for all molecules for which Eqs. (1) and (2) apply.

This can be tested via experimental values[9] of $(\frac{2}{9})D_e l_e^2/k_e^3$ and $(\frac{1}{6})D_e m_e/k_e^2$ obtained from spectroscopic data. The accuracy of the data of Ref. 9 is discussed there (±1 in the next to last digit listed). It is sufficiently accurate to provide a significant test of Eqs. (7) and (8). As GP showed,[8,10] a plot of experimental values of a_1^2/Δ versus a_2/Δ is not a single point. In fact, it has a rather broad scatter, considerably broader than one should expect from experimental data scatter.[9] This scatter is what led to their conclusion that Eqs. (1) and (2) are only moderately well satisfied. Figure 1(a), however, shows that Eqs. (1) and (2) are rather well satisfied for the 88-molecule subset in which neither atom is a halogen or in which both atoms are halogens. The scatter is again greater than one should expect from experimental data scatter,[9] but considerably smaller than one finds in Fig. 2 of Ref. 7. We find that $a_l^2/\Delta = 0.84(0.16)$ and $a_2/\Delta = 0.51(0.14)$, where the numbers given are averages with standard deviations in parentheses. That is, the average values are close to the point given by the universal constants $a_1^2/\Delta = \frac{8}{9}$ and $a_2/\Delta = \frac{1}{2}$, as determined[11] from Eqs. (7) and (8), and the standard deviations are small. Note that for this subset the charge transfer is not large. This agreement with the universal constants is consistent then with our discovery[1–6] of a universal energy relation for metallic or covalent bonds where, of course, the charge transfer is zero or small. Now this is a very difficult test for any energy relation, because it requires that both *third* and *fourth* energy derivatives at equilibrium be predicted accurately. Tests are in progress for the zeroth derivative curves, i.e., for $E(R)$. They suggest that for these molecules $E(R)$ is of the universal form to the same high accuracy that we found for solids.[1–6]

In Fig. 1(b) for the remaining 62 diatomics which contain a single halogen atom we find $a_1^2/\Delta = 1.66(0.44)$ and $a_2/\Delta = 1.08(0.30)$. This is then the origin of most of the average shift and scatter seen by GP (Ref. 10) for the 150 molecules. We now see that the apparent lack of universality is due primarily to those diatomics where the charge transfer is relatively large. This is perhaps to be expected, because in metallic and covalent solids, where $E^*(a^*)$ was discovered,[1,5–6] $E(R)$ is largely exponential in form since screening densities and electronic wave function overlaps tend to fall off exponentially with increasing R. When there is a net charge transfer δZ between the two atoms of the diatomics there is a Coulomb potential $-(\delta Z)^2/R$ component which cannot be well represented by the experimental nature of an $E^*(a^*)$ derived for metallic and covalent interactions in solids.

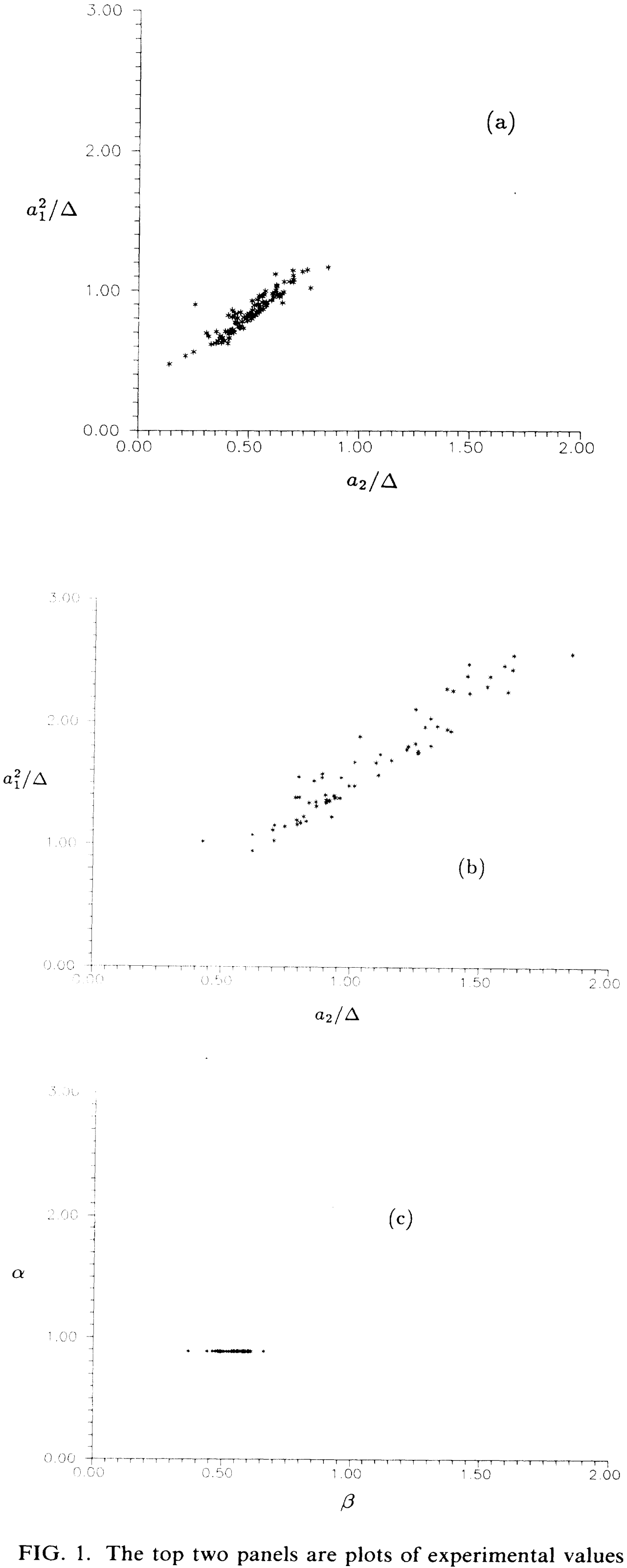

FIG. 1. The top two panels are plots of experimental values of a_1^2/Δ vs a_2/Δ [see Eqs. (3)–(8)] for (a) the 88 diatomic in which neither atom is a halogen atom or in which both atoms are halogens; (b) the remaining 62 diatomics which do contain a single halogen. Panel (c) is a plot of α vs β [see Eqs. (14) and (15)] for the set of 62 halogen-containing diatomics.

However, this does suggest a relatively simple generalization of the universal energy relation to partially ionic, partially covalent bonds. Since the universal energy relation seems to do well for covalent and metallic interactions in solids and diatomic molecules, we propose simply adding a Coulombic term to the universal form for partially ionic bonds. The presumption then is that the covalent part of the partially ionic bond can be represented well by the universal form. Thus for partially ionic bonds we have

$$E(R)=CE^*(a^*)-(\delta Z)^2/R \ , \tag{9}$$

where

$$a^*=(R-R_e')/l \ , \tag{10}$$

and R_e' is the interatomic separation at which the covalent energy component is a minimum, where $R_e' \geq R_e$. Here C, R_e', and l are determined by $E(R_e)=-D_e$, $[dE(R)/dR]_{R_e}=0$, and Eq. (3).

Now we will apply Eqs. (9) and (10) to the data[9] for the 62 halogen-containing diatomics, which is a most difficult test as shown by Fig. 1(b). If we combine Eqs. (9) and (10) with Eqs. (3)–(6), clearly a_1^2/Δ and a_2/Δ will now depend on δZ. This is consistent with the scatter shown in Fig. 1(b). One can in general recover the universal constants of Eqs. (7) and (8) as

$$\alpha \equiv \frac{(a_1^2/\Delta)_{\text{expt}}}{(a_1^2/\Delta)_{\text{theor}}}(\tfrac{2}{9})[d^3E^*(a^*)/da^{*3}]_0^2 \tag{11}$$

and

$$\beta \equiv \frac{(a_2/\Delta)_{\text{expt}}}{(a_2^2/\Delta)_{\text{theor}}}(\tfrac{1}{6})[d^4E^*(a^*)/da^{*4}]_0 \ . \tag{12}$$

Here the subscripts expt and theor refer to experimental and theoretical values respectively. We will now plot α versus β, computing $(a_1^2/\Delta)_{\text{theor}}$ and $(a_2/\Delta)_{\text{theor}}$ from Eqs. (9) and (10), and compare the scatter to Fig. 1(b). If it were to be decreased, then one could presume that the additional scatter of Fig. 1(b) is due to the ionic interaction. Further, one could presume that Eqs. (9) and (10) successfully account for the ionic interaction.

We need first to specify the charge transfer δZ. There are several empirical expressions in the literature relating δZ to, e.g., electronegativity differences,[12] dipole moments,[12], and dielectric properties[13] (for more recent work, see, e.g., Ref. 14). Let us consider the alkali halides for which $a_1^2/\Delta=2.081(0.306)$ and $a_2/\Delta=1.296(0.224)$. If we determine δZ from experimental dipole moments[12] as listed in Table I, we find $\alpha=1.178(0.218)$ and $\beta=0.710(0.153)$ for the alkali-halide molecules. These values are much closer to the universal constants of $\alpha=\frac{8}{9}$ and $\beta=\frac{1}{2}$ and the scatter is significantly reduced. This does suggest that ionic interactions are an important source of the shift and scatter in Fig. 1(b). However, the different empirical approaches give somewhat different δZ values, as can be seen in Table I. Remember that if there is any covalent component, the charge transfer is not precisely definable due to wave-function overlap. This is perhaps one of the reasons for the variation in Table I. It is important for this test therefore to have an internally consistent approach. We accomplish that by defining δZ so that the predicted a_1^2/Δ agrees exactly with the experimental value.

Then we test in two ways. First, we look to see if the scatter in β values is greater or lesser than that of a_2/Δ in Fig. 1(b). Another way of describing this test is to say that we specify δZ so that the predicted $[d^3E(R)/dR^3]_{R_e}$ agrees with the experimental value, and than we

TABLE I. Charge transfers for alkali halides.

Molecule	Pauling (Ref. 12)	Dipole (Ref. 12)	Universal (this work)	Dielectric (Ref. 13)
LiCl	0.63	0.73	0.82	0.90
LiI	0.43	0.65	0.67	0.89
NaBr	0.59	0.76	0.77	0.93
NaCl	0.67	0.79	0.83	0.94
NaI	0.47	0.71	0.65	0.93
KBr	0.63	0.78	0.88	0.95
KCl	0.70	0.80	0.91	0.95
KF	0.92	0.82	0.90	0.96
KI	0.51	0.74	0.80	0.95
RbBr	0.63	0.77	0.90	0.96
RbCl	0.70	0.78	0.94	0.96
RbF	0.93	0.78	0.91	0.96
RbI	0.51	0.75	0.82	0.95
LiF	0.89	0.84	0.84	0.92
NaF	0.91	0.88	0.88	0.95
CsBr	0.67	0.78	0.96	
CsCl	0.73	0.74	0.99	
CsF	0.93	0.70	0.93	
CsI	0.55	0.74	0.90	

ask how well $[d^4E(R)/dR^4]_{R_e}$ is predicted. Secondly, we see whether the resultant δZ values are consistent with those predicted by others.[12,13]

The results of the first test[11] are shown in Fig. 1(c). There we have plotted α versus β for the 62 halogen-containing diatomics. Here we find $\alpha=\frac{8}{9}$ and $\beta=0.55(0.05)$. Thus β is much closer to the universal constant $\frac{1}{2}$ than it was in Fig. 1(b). In the latter case $a_2/\Delta=1.08(0.30)$, as noted above. This suggests that the scatter and shift of the points in Fig. 1(b) and in Fig. 2 of Ref. 7 was indeed primarily due to ionic interactions. Further, it suggests that these ionic interactions are reasonably well represented by Eqs. (9) and (10).

Results of the second test can be found in Table I. δZ values for alkali-halide diatomic molecules are available from several different schemes, and they can be compared with those obtained here. We find that the δZ values obtained here (labeled universal in Table I) are not inconsistent with others based on electronegativity differences[12] (labeled Pauling in Table I), dipole moments,[12] or dielectric properties.[13] This provides additional confidence in our procedure. Incidentally, we are not claiming our δZ's are any better or worse than the others. Rather, as discussed above, our δZ's are internally consistent with our approach, which is based on spectroscopic data. This consistency is important to our goal of testing the validity of the universal energy relation for diatomic molecules.

In summary, we have found that spectroscopic tests of the universal energy relation do not suggest a limitation due to the diatomic configuration. In fact, the 88-molecule subset in which neither atom is a halogen or where both atoms are halogens is well described by the universal energy relation. This is not true of the other 62 molecules which do contain a halogen atom. With the simple addition of a Coulombic term to the universal form, even that 62-molecule subset is well described. This suggests that it is the ionic interaction rather than the diatomic configuration which does not fall within the universal energy relation. This makes sense because the universal energy relation was discovered for metals and covalent semiconductors, solids for which interactions fall off primarily exponentially, not Coulombically. We now have a simple expression which includes partially ionic, partially covalent bonds. The covalent part is described by the universal energy relation, the same as for solids. thus the universal energy relation for solids does not apply to the form of the covalent part of the energy relation for diatomic molecules. It should be noted that this entire study deals with higher-energy derivatives at equilibrium. One might well wonder about universality far from equilibrium. An investigation of this very interesting question is currently under way.

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[10] See Fig. 2 of Ref. 7.

[11] For definiteness in this test, we represent $E^*(a^*)$ by the Rydberg function: $E^*(a^*)=-(1+a^*)e^{-a^*}$. This has been shown (see Refs. 1–6) to be an accurate approximation to the universal energy relation.

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