Global expression for representing diatomic potential-energy curves

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We propose a three-parameter expression that gives an accurate fit to diatomic potential curves over the entire range of separation for charge transfers between $0 \leq \delta Z \leq 1$. It is based on a generalization of the universal binding-energy relation [J. R. Smith *et al.*, Phys. Rev. A **39**, 514 (1989)] with a modification that describes the crossover from a partially ionic state to the neutral state at large separations. The expression is tested by comparison with first-principles calculations of the potential curves ranging from covalently bonded to ionically bonded. The expression is also used to calculate spectroscopic constants from a curve fit to the first-principles curves. A comparison is made with experimental values of the spectroscopic constants.

I. INTRODUCTION

It has long been of interest to determine whether a simple analytic relation exists that represents the binding-energy relation of diatomic molecules over a wide range of separations.[1] If such a relation were known, then it could greatly facilitate simulation of molecular energetics. In the following we will provide such a relation and test it against first-principles calculations and experiment. Rose, Smith, and Ferrante[2,3] have demonstrated that there exists a "universal" binding-energy relation which accurately describes the shape of the binding-energy curves for metallic and covalent bonds in adhesion,[4,5] chemisorption,[6] cohesion in metals,[7] diatomic molecules,[8] and even of nuclear matter.[9] Graves and Parr[10] devised a test of universality for diatomic molecules based on the highly accurate experimental values of spectroscopic constants. They constructed several parameters, consisting of combinations of spectroscopic constants, which were predicted to be constant if universality existed. In a test of 150 molecules they found considerable scatter in the parameters because their sample included both covalently and partially ionically bonded molecules. Recently, Smith *et al.*[11] showed that in testing for universality it was necessary to separate the molecules into two distinct classes: covalent and partially ionic. They found that the parameters for the 88 covalently bonded molecules investigated clearly demonstrated universal behavior. Tellinghuisen *et al.*[12] reported results leading to a similar conclusion. Furthermore, Smith *et al.* showed that the addition of an ionic term to the universal equation, in the case of the remaining 62 partially ionic molecules, eliminated most of the scatter in the appropriate test parameters. Thus, if the effect of charge transfer is included in a generalized universal equation, *all* 150 diatomic molecules exhibit universal behavior. Additionally, the charge-transfer values found from the universal equation are comparable to those predicted by other means.[11]

The above tests of universality[10–12] probed the relationship only in the vicinity of the minimum at the equilibrium separation. This is a severe test, since predictions of third and fourth derivatives were involved. However, the results of Refs. 2 and 11 suggest that it may be possible to find a simple globally accurate functional representation for potential curves away from the vicinity of the minimum. In this study we examine the use of a three-parameter form, based on the results of Refs. 2 and 11, to represent the potential curves for a number of diatomic molecules obtained from first-principles calculations. The molecules investigated range from covalently bonded to ionically bonded. Finally, we show that this three-parameter functional form can be used to determine the spectroscopic constants from first-principles calculations, and that these compare well with experimental values.

II. ANALYSIS

The authors of Ref. 2 found that the binding-energy relation for diverse physical phenomena could be scaled, i.e., written in a functional form

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

where $a^* = (R - R_e)/l$, $E(a^*)$ is a universal function of a^*, R is the separation, R_e is the equilibrium separation, D_e is the binding energy, and l is a scaling length defined as

$$l = \left[D_e \Big/ \left[\frac{d^2 E}{dR^2} \right]_{R_e} \right]^{1/2} . \tag{2}$$

This particular choice for the scaling length, l, was selected since it could be calculated from experimentally measurable quantities. Although, universality, i.e., scaling, is independent of the functional form used to represent it, Rose et al.[2] found that the Rydberg function,

$$E^*(a^*) = -(1+a^*)\exp(-a^*) \qquad (3)$$

was a good representation of the potential curves for covalently bonded materials. In fact, Smith et al.[11] found that Eq. (3) represented experimental spectroscopic parameters well for the 88 covalently bonded molecules out of the 150 molecules examined. As might be expected, this expression was found to be inadequate for the

remaining 62 ionically bonded molecules. Smith et al.[11] proposed a simple extension of Eq. (3) for bonding with charge transfer (atomic units are used throughout)

$$E(R) = -C(1+a^*)\exp(-a^*) - \delta Z^2/R , \qquad (4)$$

where $a^* = (R - R_e')/l$, C is the well depth for the Rydberg function, l and R_e' are respectively the scaling length and the equilibrium position for the Rydberg function, and δZ is the charge transfer. We note that there are only two independent fitting parameters if we require that $E(R_e) = -D_e$ and $(dE/dR)_{R=R_e} = 0$. It was found that[11] Eq. (4) represented well the experimental spectroscopic constants for the 62 partially ionically bonded

TABLE I. Charge-transfer values from spectroscopic constants (Ref. 30).

Molecule	Pauling (Ref. 14)	Dipole (Ref. 14)	Universal (This work)	Dielectric (Ref. 31)	C/D_e
CuF	0.668	0.688	0.616	0.766	0.310
CuCl	0.261		0.567	0.746	0.437
CuBr	0.183		0.491	0.735	0.541
CuI	0.086		0.495	0.692	0.546
AgF	0.668	0.653	0.520	0.894	0.470
AgCl	0.261	0.521	0.441		0.623
AgBr	0.183		0.446	0.850	0.618
AgI	0.086		0.324	0.770	0.773
BeF	0.790		0.617		0.378
BeCl	0.430		0.506		0.552
MgCl	0.555		0.423		0.648
CaF	0.895		0.802		0.178
CaCl	0.632		0.664		0.379
SrF	0.895		0.807		0.223
BaF	0.910		0.878		0.190
CF	0.430	0.106	0.552		0.407
SiF	0.702		0.618		0.399
GeF	0.702		0.605		0.410
SnF	0.702		0.396		0.765
PbF	0.702		0.474		0.573
BF	0.632	0.082	0.769		0.176
BCl	0.221		0.681		0.316
BBr	0.148		0.438		0.679
AlF	0.790	0.193	0.849		0.136
AlCl	0.430	0.147	0.795		0.200
AlBr	0.345		0.723		0.283
AlI	0.221		0.645		0.389
GaF	0.763	0.287	0.815		0.140
GaCl	0.387		0.797		0.190
GaBr	0.302		0.728		0.274
GaI	0.183		0.604		0.426
InF	0.734	0.357	0.780		0.189
InCl	0.345	0.329	0.765		0.235
InBr	0.261		0.711		0.303
InI	0.148		0.629		0.410
TlF	0.702	0.419	0.714		0.252
TlCl	0.302	0.378	0.666		0.344
TlBr	0.221	0.357	0.601		0.430
ScF	0.838		0.690		0.394
ScCl	0.514		0.450		0.618
YF	0.859		0.698		0.425

molecules. Also, reasonable estimates of δZ for the alkali halides[11] were obtained from application of Eq. (4) to the spectroscopic data, as compared with estimates from dipole moments, Pauling electronegativities and dielectric constants. In Table I we present δZ values for the remaining partially ionic halide molecules not reported in Ref. 11.

Equation (4) differs from a form used to represent the binding energy of ionic solids, the Born-Mayer potential.[13] The Born-Mayer potential consists of two terms, an exponential term which is completely repulsive and a second term which is identical to the ionic attractive term in Eq. (4). Use of the Rydberg function in Eq. (4) instead of the repulsive exponential allows for the possibility of some covalent bonding and thus fits the Pauling[14,15] description of a bond as being partially ionic and partially covalent. This is more realistic from a physical standpoint than the Born-Mayer potential.

For the purpose of representation of first-principles potential curves at large interatomic separations, Eq. (4) has a basic limitation in that it is referenced to dissociation into two ions at infinite separation, whereas the experimental dissociation energy D_e is referenced to two neutrals. Thus, when an ionic diatomic dissociates, a crossover to the neutral state occurs when it becomes energetically favored over the ionic state.[16,17] In the crossing region (Fig. 1) the first-principles potential curves include a mixture of these two states. This suggests that the second term in Eq. (4) be modified in order to represent first-principles results not only in the vicinity of the equilibrium separation, but also at intermediate and large separations. We propose the following analytic form that has ionic, $(1/R)$, behavior near the equilibrium radius and

converts to an exponential decay in the vicinity of $R > R_0$,

$$-\delta Z^2 \{ 1 + \exp[\alpha(R - R_0)] \}^{-1}/R , \qquad (5a)$$

yielding

$$E(R) = -C(1 + a^*)\exp(-a^*)$$
$$-\delta Z^2 \{ 1 + \exp[\alpha(R - R_0)] \}^{-1}/R , \qquad (5b)$$

where α is a parameter obtained from fitting and R_0 is the crossing radius. Note that there are three independent parameters remaining if we impose the conditions $E(R_e) = -D_e$ and $(dE/dR)_{R_e} = 0$ as in Eq. (4), and provided that we have an independent method for specifying R_0.

The crossing radius R_0 equals the classical value[16,17] $1/(I - A)$ for $\delta Z = 1$. Since there is no analytic expression for R_0 when $\delta Z < 1$, as a reasonable first-order approximation we choose a linear interpolation in δZ^2 between the equilibrium radius R_e and the classical value $1/(I - A)$:

$$R_0 = R_e(1 - \delta Z^2) + \delta Z^2/(I - A) , \qquad (6)$$

where I is the ionization potential of the electropositive ion and A is the electron affinity of the electronegative ion. We will demonstrate that Eq. (5b) with R_0 given by this functional form accurately represents the shape of the potential-energy curves for a variety of different molecules with varying degrees of ionicity. The quality of the curve fits to the first-principles potential curves will illustrate the appropriateness of this choice of R_0. As an additional test of these expressions, we will also use the fitting parameters obtained from this procedure to calculate the spectroscopic constants for the molecules. To reiterate, we have constructed an expression that mimics the physical behavior of the binding, namely: a repulsive core, covalent and ionic binding, and the crossing to the neutral state at large separation.
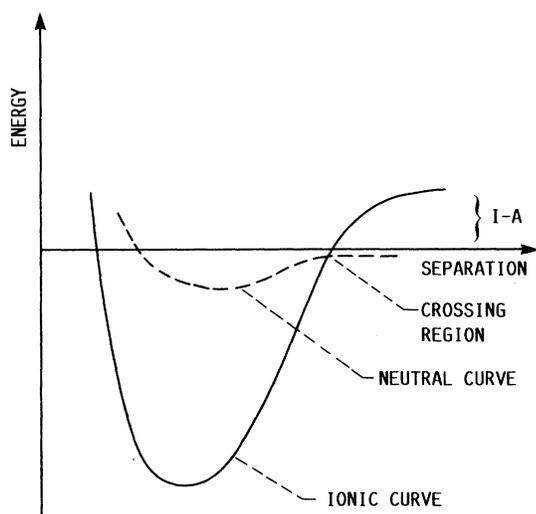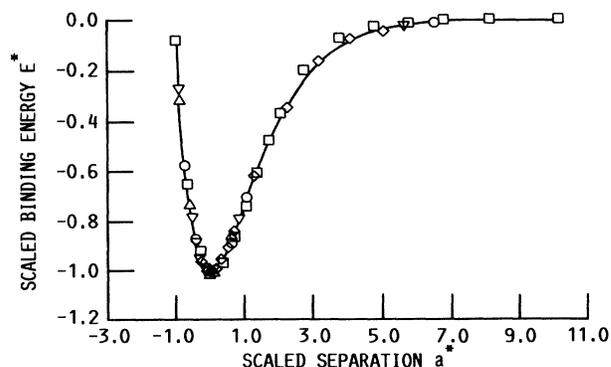

FIG. 1. Schematic of the ionic and neutral potential curves showing the crossing between states. I is the ionization potential of the electropositive ion and A is the electron affinity of the electronegative ion.

FIG. 2. Scaled potential curves showing the agreement with the Rydberg function [Eq. (3)] for Li_2, Be_2, InH, PbO^+, and SnO^+.

III. RESULTS

We sort the potential curves into three categories. First, are those with negligible charge transfer [Li$_2$,[18] Be$_2$, [19]InH,[20] PbO$^+$,[21] SnO (Ref. 21)] and for which the Rydberg function [Eq. (2)] is a good representation. The second set includes the alkali hydrides [LiH[22], NaH (Ref. 23)], and the hydrogen-halogen diatomics [HCl,[24] HF,[24] HBr (Ref. 24)] with a range of charge transfers and thus constitute an intermediate category. Finally we have those halides [AlF,[25] AlCl,[25] LiF (Ref. 26)] with large transfers where Eq. (3) is clearly inadequate.
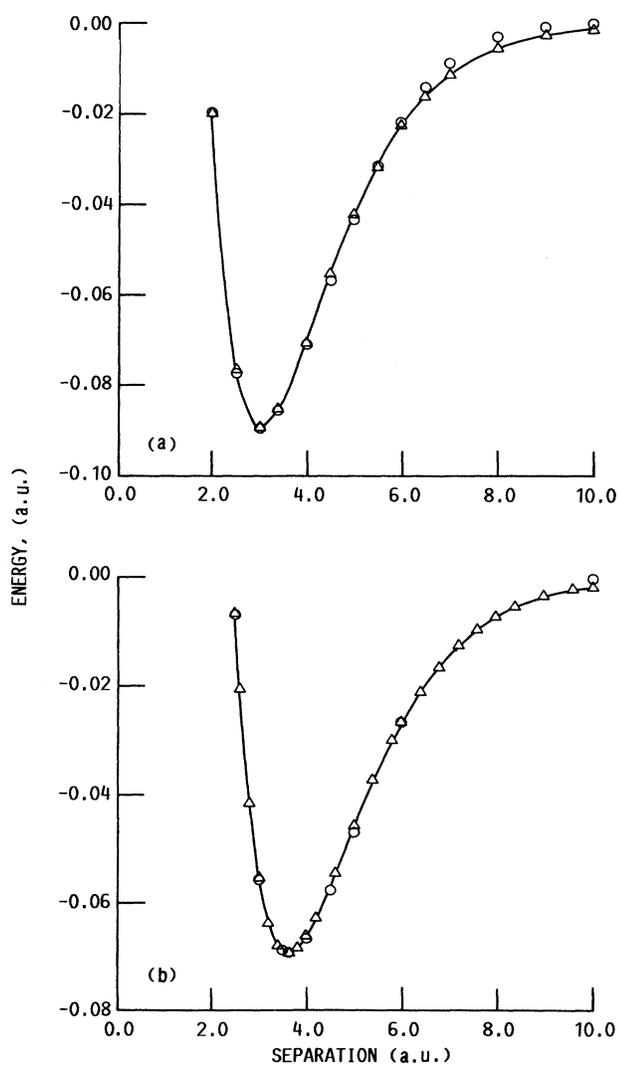
We have obtained the three parameters in Eq. (5b) by

fitting with a Simplex method to first-principles total-energy curves for LiH, NaH, HF, HCl, HBr, AlF, AlCl, and LiF (Figs. 2–5). The selection of first-principles results was based on the necessity to span a wide range of charge transfers and separations from the compressive to
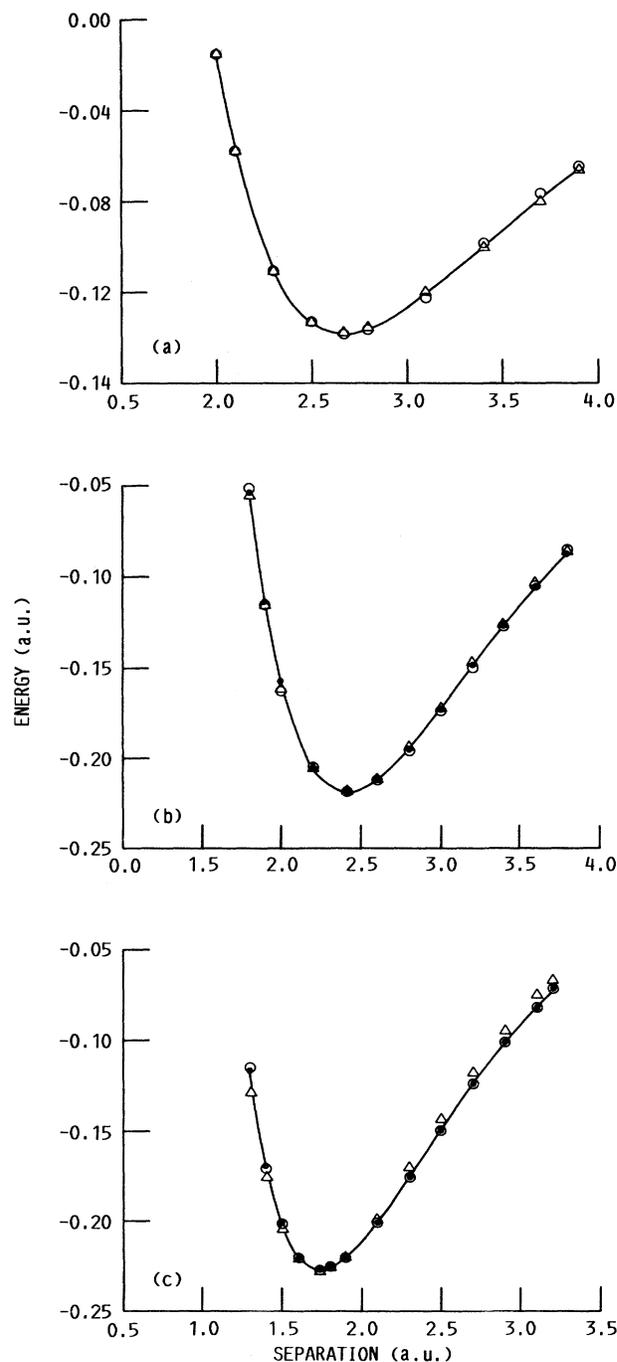

FIG. 3. A comparison between first-principles potential curves (O) and the Rydberg function ($\triangle$) [Eq. (3)]. (a) LiH, (b) NaH.
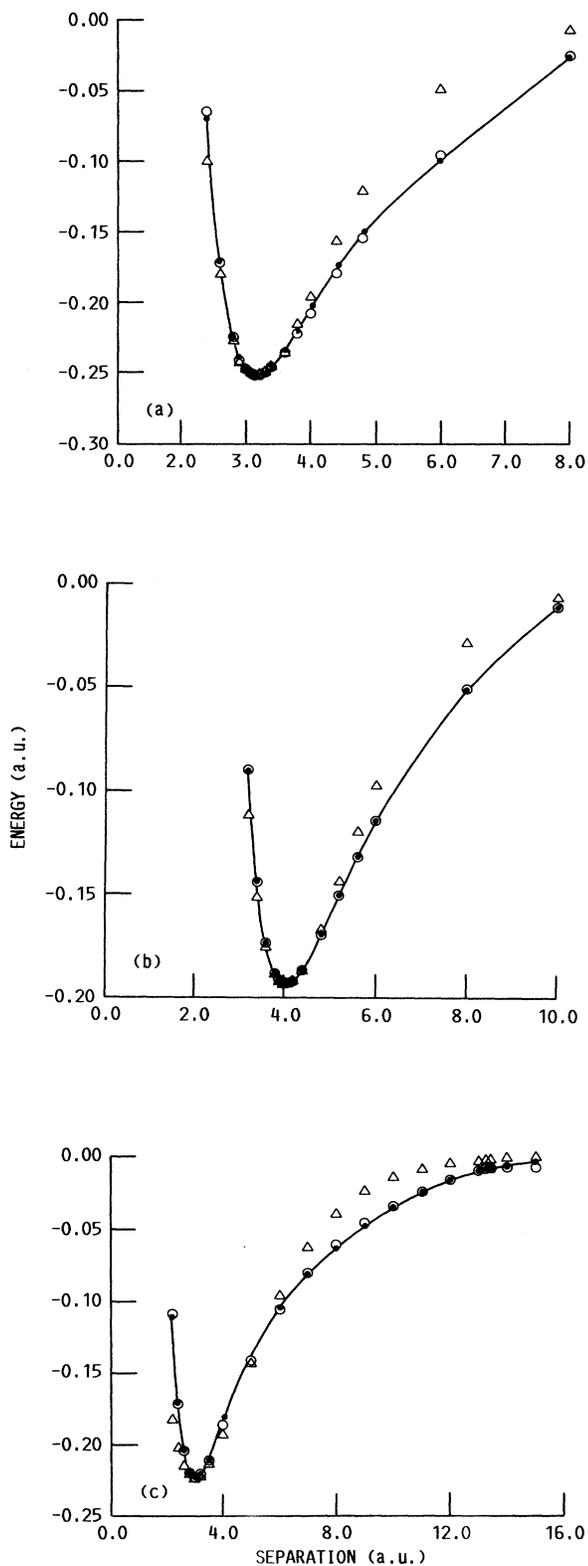

FIG. 4. A comparison between first-principle potential curves (O), the Rydberg function [Eq. (3)] ($\triangle$), and the present work (-●-) in the intermediate charge-transfer region [Eq. (5a)]. (a) HBr, (b) HCl, (c) HF.

the tensile regions as a test of Eqs. (5) and (6) and the availability of calculations for a large range of separations. These criteria are necessary in order to test the various terms in Eq. (5b) which dominate in different regions of the potential curves.

We now make several observations concerning these results. First, we note that the Rydberg function gives an excellent fit to the scaled energy curves for the first set (Fig. 2) and for the unscaled energy curves [Eqs. (1) and (2)] for LiH and NaH (Fig. 3) as might be expected. In the next set (HBr, HCl, HF) (Fig. 4) the ionic term of Eq. (5a) makes an increasingly important contribution to the energy as δZ increases through the set. Thus, the Rydberg function yields the best fit for HBr, while Eq. (5b) is slightly better for HCl ($\delta Z = 0.062$) and substantially better for HF ($\delta Z = 0.16$). However, note that we do not have values for large R for these molecules. Finally, we see that for the ionic molecules (LiF, AlCl, and AlF) Eq. (5b) provides an excellent fit to the potential curves over the entire range of separations. Values of the fitting parameters for LiH, NaH, HCl, HF, AlF, AlCl, and LiF are given in Table II.

We found from the curve fits for LiF, AlCl, and AlF that the contribution from the exponential in Eq. (5a) was negligible near the minimum and thus this term had an $1/R$ dependence in this region. Thus, for this type of molecule the exponential function in the ionic part of the equation models the crossover from the ionic state to the neutral state with an exponential decay in the region for $R > R_0$. For these molecules, therefore, the simple identification of δZ as the charge transfer has validity.

As δZ approaches zero, Eq. (5b) approaches the Rydberg function. For this case, the ionic term provides a negligible contribution to the binding energy as shown by Figs. 3 and 4.

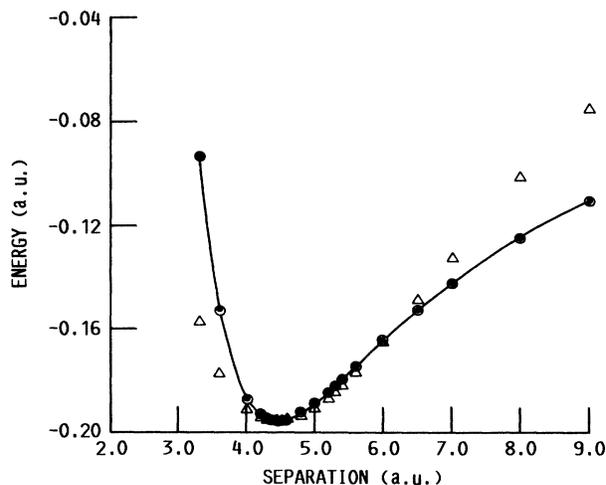The simple identification of δZ in Eq. (5a) as the

FIG. 5. A comparison between first-principles potential curves ($\bigcirc$), the Rydberg function [Eq. (3)] ($\triangle$), and the present work [Eq. (5a)] (-●-) for ionic molecules. (a) AlF, (b) AlCl, (c) LiF.

FIG. 6. A comparison between the Kim-Gordon potential curve for Na^+Cl^- (Ref. 27) ($\bigcirc$), the Rydberg function [Eq. (3)] ($\triangle$), and the present work [Eq. (4)] (-●-)

TABLE II. Values for parameters in Eq. (5a) (atomic units).

	1	R_e'	α	δZ	C	R_0
LiF	0.708 756	3.669 01	0.490 93	0.823 405	0.22 4177	10.2247
AlCl	0.806 112	4.371 39	1.030 63	0.779 209	0.050 5117	8.559 83
AlF	0.661 312	3.4315	1.51 103	0.777 838	0.068 994	7.614 48
HF	0.612 931	1.791 03	8.782 71	0.160 466	0.219 587	1.756 96
HCl	0.686 376	2.420 09	11.48 06	0.062 4222	0.218 012	2.410 73
HBr	0.702 877			0.0		
NaH	1.150 67			0.0		
LiH	1.112 33			0.0		

charge transfer is questionable for the molecules with intermediate values of δZ, (i.e., HCl, HF), since the exponential in Eq. (5a) is not small and therefore, the "ionic term" differs substantially from $1/R$ behavior. Thus, for
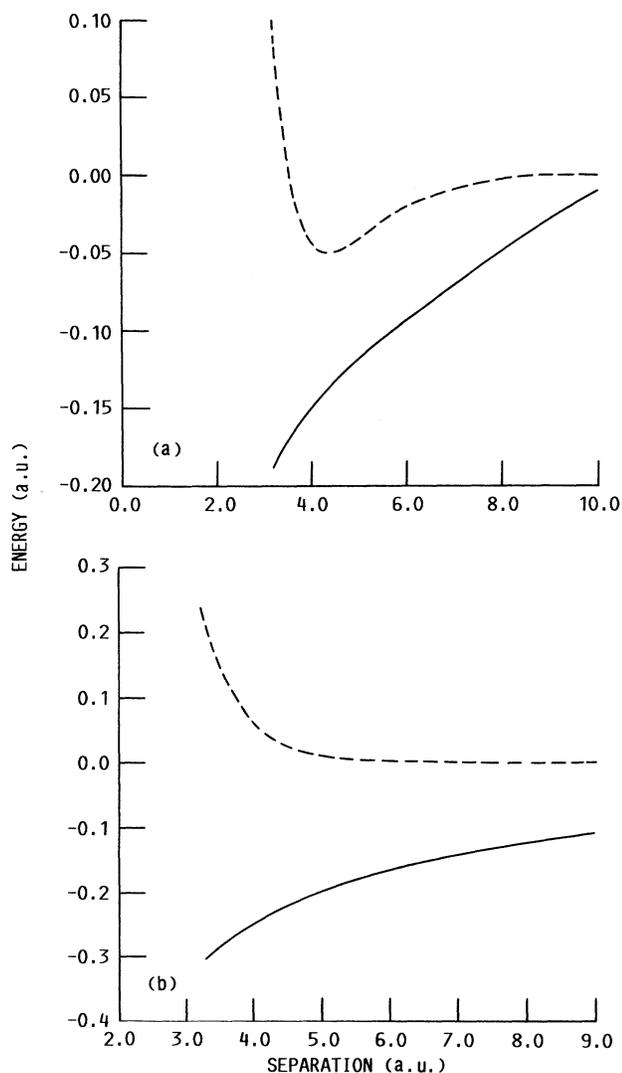

FIG. 7. Decomposition of the potential curves from the present work into the covalent part ($- - -$) and the ionic part ($\underline{\hspace{1cm}}$). (a) AlCl [Eq. (5a)], (b) Na^+Cl^- [Eq. (4)].

these Eq. (5b) should be regarded as an interpolation formula which gives an accurate fit to the potential-energy curves for intermediate values of δZ.

As a test of the ionic portion of Eq. (5a), we examine the calculations of Kim and Gordon[27] for diatomic Na^+Cl^-. They use a simple overlap of ionic wave functions and density-functional theory with no electronic relaxation included for calculation of the potential curve. Thus with a purely ionic second term Eq. (4), we obtain a highly accurate fit (Fig. 6) giving $\delta Z = 1.0$, $C = 1.26 \times 10^{-5}$, and $R_e' = 9.39$. From the value of the constants we see that the result is very close to a Born-Mayer potential. Thus, our procedure gives an excellent fit and the correct charge transfer for a calculation that is purely ionic by construction. In Fig. 7 we compare the covalent and ionic parts of our fits to the potential curves for AlCl and Na^+Cl^- [Eq. (4)]. We can readily see that for AlCl the covalent part has an attractive well, whereas for Na^+Cl^- it is essentially an exponential repulsion. It is interesting to note that the absence of electronic rearrangement in the Kim-Gordon calculation suggests that
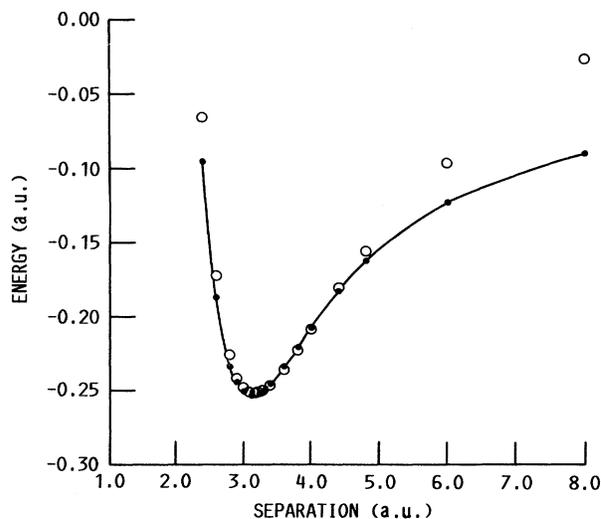

FIG. 8. A comparison between first-principle potential curves calculated for AlF ($\bigcirc$) and the present work (-$\bullet$-) using spectroscopic constants for calculating the parameters in Eq. (4).

TABLE III. Diatomic spectroscopic constants (cm^{-1}). Values in parentheses are experimental values (Ref. 31).

	ω_e	B_e	α_e	$\omega_e x_e$
LiF	946.6 (910.3)	1.315 (1.345)	0.01604 (0.02029)	7.819 (7.929)
AlCl	502.8 (481.3)	0.2404 (0.2439)	0.001427 (0.001611)	2.24 (1.95)
AlF	824.8 (802.2)	0.5371 (0.5525)	0.004144 (0.004984)	4.756 (4.77)
HF	4368.6 (4138.3)	20.97 (20.96)	1.119 (0.798)	281.93 (89.88)
HCl	3573.4 (2991)	10.59 (10.59)	0.3489 (0.3072)	106.2 (52.82)
HBr	2725.1 (2649)	8.471 (8.465)	0.2428 (0.2333)	56.17 (45.22)
NaH	1194.7 (1172.2)	4.7901 (4.901)	0.1258 (0.1353)	21.61 (19.72)
LiH	1471.1 (1405.7)	7.534 (7.513)	0.1868 (0.2132)	25.37 (23.20)

inclusion of electronic relaxation leads to the attractive part of the first term in Eqs. (4) or (5b).

Next we compare the first-principles potential curves to Eq. (4) with constants obtained from the spectroscopic constants for AlF (Fig. 8). This molecule was selected for comparison, since there is close agreement between the experimental and theoretical values of D_e and R_e. As might be expected the agreement near the minimum is quite good by construction. Surprisingly, the agreement is rather good over a fairly large separation range.

We make one final comparison, namely, we calculate the spectroscopic constants, ω_e, B_e, α_e, and $\omega_e x_e$ (Refs. 28 and 29) as defined by

$$\omega_e^2 = 2.642\,829 \times 10^7 k_e/m , \qquad (7)$$

$$B_e = 4.561\,3274 \times 10^{-6} \omega_e^2/(4\Delta D_e) , \qquad (8)$$

$$\alpha_e = 6(1 + a_1)B_e^2/\omega_e , \qquad (9)$$

$$\omega_e x_e = -1.5 B_e(a_2 - 1.25 a_1^2) , \qquad (10)$$

where

$$k_e \equiv \left[\frac{d^2 E}{dR^2}\right]_{R_e} ,$$

$$l_e \equiv \left[\frac{d^3 E}{dR^3}\right]_{R_e} ,$$

$$m_e \equiv \left[\frac{d^4 E}{dR^4}\right]_{R_e} ,$$

$$\Delta \equiv \frac{k_e R_e^2}{(2D_e)} ,$$

$$a_1^2 \equiv \left[\frac{l_e R_3}{3k_e}\right]^2 ,$$

$$a_2 \equiv \frac{m_e R_e^2}{(12k_e)} ,$$

m is the reduced mass, D_e is the binding energy in atomic units, and R_e is the equilibrium spacing in atomic units. The spectroscopic constants have units of cm^{-1}. In Table III we show the results of using our fitting parameters to calculate the spectroscopic constants compared with experimental values obtained from Ref. 30. First, we note that the values we obtain for these constants are only as good as the first-principles calculations used for fitting. We also note that these are values obtained from a global fit to the potential curves and not from values of the curve near the minimum. With these provisos we feel that the agreement is quite good, since we are extracting higher-order derivatives at the minimum from a global fit to the potential curves.

In conclusion, we have found a three-parameter functional form which accurately represents the potential curves for diatomics obtained from first-principles calculations, over a wide range of charge transfers and spacings. This expression has a simple interpretation in terms of Pauling's description of partially ionic and partially covalent bonding. Good agreement is obtained between the spectroscopic constants extracted from this procedure and the experimental values of the spectroscopic constants.

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