

Comment on “Universal Reduced Potential Function for Diatomic Systems”

Since quantum mechanics fails on a low-parameter universal function for potential energy curves (PECs), searches for a universal function (UF) remain important [1–7]. Xie and Hsu recently published a Letter [1] on a universal reduced potential function for diatomic systems. This Comment will show their claims can be disproved. Their 200 bonds between atoms with closed *S*-type shells cover the columns I, II, and VIII (noble gases) of the periodic table. Since column VII with univalent atoms, covering 50% of the common bonds, is excluded, while 56% of the uncommon bonds with noble gases are included [1,2], their claim to have found a universal function is invalid. If it were valid, its universal bond is typified with bound inert gases, which are nonbonding. This is a self-contradictory result. Further remarks that are pertinent follow below.

Reference [1] uses (i) Dunham’s potential, scaled by D_e , giving covalent Sutherland parameter [3–7]

$$\Delta = \Delta_{\text{cov}} = \frac{1}{2}k_e r_0^2 / D_e \quad (1a)$$

and (ii) Varshni’s procedure with F and G [7]. For the UF, smooth $G(F)$ as well as $F(\Delta)$ and $G(\Delta)$ plots should encompass observed constants [3–7]. However, for 300 bonds with H and atoms in all columns I–VIII, $F(\Delta)$ and $G(\Delta)$ are scattered; only $G(F)$ is relatively smooth [4]. While [3–7] all find scattering for many bonds in [1], Xie and Hsu give smooth plots in their Fig. 2 [1]. To understand this contradiction, Fig. 1 here expands on $G(\Delta)$ for $G \leq 100$ [1] with data [5] added. The scattering in Fig. 1, reported in [3–7], is obscured in [1] by data compression to give seemingly smooth plots in their Fig. 2, whereas in reality Fig. 1 shows that their plot is not smooth at all.

The full line in Fig. 1 reveals that their 200-bond fit $G = 7, 2422\Delta$ [1] is rather poor. In fact, it hardly differs from analytical result $G = 7, 3333\Delta$ for Rydberg’s not-universal function [7]. In Xie and Hsu’s Letter [1], the large gaps for halogen bonds [5] (see Fig. 1) are avoided by bond selection but this leads to a self-contradictory universal bond.

Reference [1] argues that, contrary to the work in Ref. [4], Eq. (1a) is a valid scaling aid. The 300-bond study in [4] reveals that the ionic Sutherland parameter

$$\Delta_{\text{ion}} = \frac{1}{2}k_e r_0^2 / D_{\text{ion}} \quad (1b)$$

with ionic energy $D_{\text{ion}} = e^2/r_0$ [5] is a better approach than Eq. (1a). In fact, for all bonds with all univalent atoms in the periodic table Δ_{ion} makes both $G(\Delta_{\text{ion}})$ and $F(\Delta_{\text{ion}})$ as smooth as $G(F)$, which probes the universal function for common bonds [4,5]. If the large gaps in Fig. 1 persist, then Δ_{cov} in Eq. (1a) and/or Dunham theory do not describe the situation accurately. With Δ_{ion} and the work in [5] omitted in Xie and Hsu’s work [1], their scaling approach based on (1a) has limitations [8].

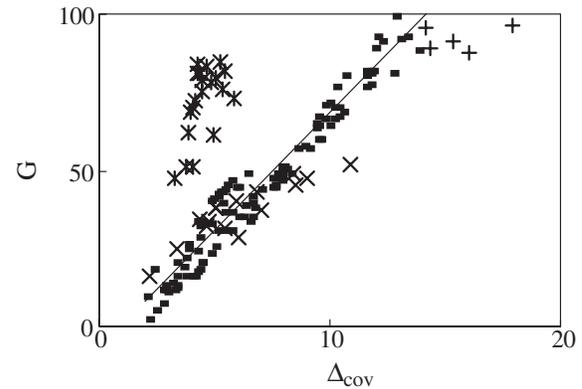


FIG. 1. $G(\Delta)$ for $G \leq 100$: data [1] (–); data [5] (+) halogens X_2 , (*) salts MX , (×) other bonds with H, M, X.

Since Δ_{ion} unifies common bonds, their unifying ionic function should at least be accurate for prototypical covalent H_2 , also in [1]. One can perform an accuracy test for H_2 using observed $r_0 = 0.7414 \text{ \AA}$ and $\omega_e = 4401 \text{ cm}^{-1}$. While the empirical fit of the 3-parameter potential in [1] gives $\omega_e = 4656 \text{ cm}^{-1}$, parameter-free ionic Kratzer potential $U_K(r) = \frac{1}{2}(e^2/r_0)(1 - r_0/r)^2 = \frac{1}{2}k_e r_e^2(1 - r_0/r)^2$ [4,6,9] gives analytically $\frac{1}{2}e^2/r_0 = 78\,500 \text{ cm}^{-1}$, $k_e = e^2/r_0^3 = 5.7 \times 10^5 \text{ dyne/cm}$, and $\omega_e = 4390 \text{ cm}^{-1}$.

With bonds between all univalent atoms unified by an ionic Kratzer-type universal function, their potential energy curves favor ionic bonding, implying that prototypical covalent structure H_2 acts like a pair of ionic structures $[H^+H^-; H^-H^+]$ [4]. This model is not self-contradictory and describes the situation and its novel implications [4,6,10] accurately.

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