

Comment on Universal Reduced Potential function for Diatomic Systems

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Finding a universal function valid for 200 bonds, Xie and Hsu [1] stated that (i), contrary to [2], the Sutherland parameter is a valid scaling factor, and (ii) ‘Based on the scaling analysis of 300 diatomic molecules, [1] pointed out [2] that the Sutherland parameter Δ can never be a universal scaling factor’, which are two inaccurate representations of [2]. Contrary to [1], I showed 25 years ago [3] that a *covalent* Sutherland parameter Δ is not universal because its *ionic* equivalent is superior [2,3]. This incorrect assessment of my work by Xie and Hsu [1] might be due to omission of refs. 2 and 3 from [4], as Xie acknowledged [5] (see also [6]). Xie’s 200-bond study [4] cited a 150-bond study [7] but not my work involving 400 bonds [2]. Xie and Hsu [1] failed to distinguish between *covalent* and *ionic* Sutherland parameters [3], an important distinction according to [8]. Ref. [1] refers to 3 parameters α , β and γ [4], needed to improve the poor QM PEC (potential-energy curve) for H_2^+ ; to align the theoretical and observed PEC, 3 parameters are known [2,3,7,8] to suffice. For scaling, a Dunham expansion [1] requires the *covalent* Sutherland parameter, $\Delta_{cov} = \frac{1}{2}k_e r_0^2 / D_{cov} = (r_0/L_2)^2$, in which appear $L_n = (n! D_{cov}/f_n)^{1/n}$ and the n^{th} force constant $f_n = d^n U(r)/dr^n$, but Xie and Hsu [1] did not even mention the better ionic alternative [2].

From first principles one can explain why scaling with the *covalent* Sutherland parameter $\Delta_{cov} = \frac{1}{2}k_e r_0^2 / D_{cov}$ (for $A+B \rightarrow AB$), used in [1,4], is less efficient than with the *ionic* $\Delta_{ion} = \frac{1}{2}k_e r_0^2 / D_{ion}$ (for $A^+ + B^- \rightarrow AB$) [2,3]. The solution of wave equations for bonds has encountered difficulty since 1930. Fixing the asymptotes as D_{cov} leaves potentials uncertain (Morse, Pekeris, Dunham...), whereas fixing the potentials (Coulomb, Kratzer) gives asymptote problems. This dilemma can be rationalized with *covalent* and *ionic* Sutherland parameters. The two are algebraically distinguished with Hooke-type Dunham $U_D(r)$ and Coulomb-type Kratzer $U_K(r)$ oscillators having asymptotes a_0 and A [2,3,9] respectively,

$$U_D(r) = a_0(1-r/r_0)^2 = a_0(1-N)^2 = a_0(N-1)^2 = \frac{1}{2}k_e r_0^2(1-r/r_0)^2 \quad (1)$$

$$U_K(r) = A(1-r_0/r)^2 = A(1-1/N)^2 = A(N^2)(N-1)^2 \quad (2)$$

Although both forms are zero at $N=1$, as Dunham’s oscillator (1) can never converge to its own asymptote a_0 , expansions are needed [9], whereas Kratzer’s form (2) invariably converges to A , even without expansions [9]. Force constants $k_e = 2D_{cov}/r_0^2$ for (1) and $k'_e = 2A/r_0^2$ for (2) determine PEC-shapes at the energy minimum.

Dunham’s primary coefficient $a_0 = \frac{1}{2}k_e r_0^2$ cannot be calculated simply from first principles and typically differs (strongly) from D_{cov} [2]. For Dunham’s (1) to be used for scaling (with a *covalent* Sutherland parameter $\Delta_{cov} = a_0/D_{cov}$), severe adaptations are needed on either side of r_0 . With a Kratzer Coulomb law $-e^2/r$ in (2) for ionic bonding (consistent with nuclear repulsion in a B-O approximation), the force constant is obtainable algebraically from first principles: $k'_e = e^2/r_0^3$ gives $A = \frac{1}{2}e^2/r_0$, which ensures that $\Delta_{ion} = \frac{1}{2}(e^2/r_0)/D_{ion}$, readily understood with classical physics. $U(r_0) = -e^2/r_0$, the *ionic* bond energy [2,3,9], gives $\Delta_{ion} \approx \frac{1}{2}$. Despite its simplicity, this mechanism yields, for so-called *covalently* bound H_2 ($r_0 = 0.7414 \text{ \AA}$), $A = \frac{1}{2}e^2/r_0 = 78300 \text{ cm}^{-1}$ and $k'_e = e^2/r_0^3 = 5.7 \cdot 10^5 \text{ dyne/cm}$, consistent with observation, even for H_2 for which the Dunham asymptote $a_0 = 79500 \text{ cm}^{-1}$ in (1) and $k_e = \omega_e/4B_e = 5.7 \cdot 10^5 \text{ dyne/cm}$. For H_2 , *ab initio ionic theory* gives vibrational frequency $\omega_e = 4390 \text{ cm}^{-1}$, near the observed 4400 cm^{-1} . This nearly *exact* result from first principles for H_2 , possible only with Kratzer’s (2), makes a physically reliable *ionic* Sutherland parameter more suitable than a *covalent* one. As this direct connection with chemical bonding is absent from [1,4], Xie and Hsu incorrectly assessed some essentials of molecular scaling related to (1) and (2), as exposed in [2,3,9].

Kratzer’s form (2) appears not only in a symmetry-reduced Hamiltonian for H_2 [9] but also in Sommerfeld’s famous double square-root equation for the H fine structure [10], later *recovered* by Dirac in QED [11]. Sommerfeld-Kratzer’s Coulomb-based universal potential $U_K(N) = \frac{1}{2}(e^2/r_0)(1-1/N)^2$ for H_2 in (2) demonstrates exactly why the prototypical molecule H_2 is for molecular spectroscopy what the prototypical atom H and Bohr’s $U_B(n) = \frac{1}{2}(e^2/r_B)(1-1/n^2)$ are for atomic spectroscopy [2]. Kratzer-type *scaling with an ionic Sutherland parameter* [2,3,9] then becomes essential, contrary to published conclusions [1,4].

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