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A Canonical Approach to Forces in Molecules

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Abstract

In a previous study, we introduced a generalized formulation for canonical transformations and spectra to investigate the concept of canonical potentials strictly within the Born-Oppenheimer approximation. Data for the most accurate available ground electronic state pairwise intramolecular potentials in H_2^+, H_2, HeH^+, and LiH were used to rigorously establish such conclusions. Now, a canonical transformation is derived for the molecular force $F(R)$ from the Hellmann-Feynman Theorem with H_2^+, the simplest molecule as molecular reference. These transformations are demonstrated to be inherently canonical to high accuracy but distinctly different from those corresponding to the respective potentials of H_2, HeH^+, and LiH. Further applications of this methodology to Mg_2, benzene dimer and to water dimer are also considered within the radial limit. The implications of these results for electrostatic model of chemical bonding will be considered and discussed using this fundamentally force-based canonical approach.

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1. Introduction

It is recognized that almost all molecular phenomena may be attributed directly or indirectly to the forces between atoms [1]. Recently, the source of chemical bonding particularly that involving the history and philosophy of covalent bonding has been reviewed [2] and describes the diversity of approaches used to consider the fundamental physical basis of chemical bonding. This included the force-based concept of chemistry [3, 4] for the electrostatic model of bonding that has been the subject of extensive consideration and acceptance. In another recently published work, by Bacskay and Nordholm [5], the origin of bonding in the simplest molecule H_2^+ has been considered supporting a mechanism proposed by Hellmann [6] that lowering of kinetic energy and associated electron delocalization are considered as the stabilization of the molecule and the key mechanism of bonding [7-9]. This conclusion was in contrast with the perspective of Slater [10], Feynman [3], Bader [11], and others who maintained that the source of stabilization of electrostatic potential energy lowering is attributed to the electron density binding regions between the nuclei. The work of Bacskay and Nordholm [5] proposes that the electrostatic model of covalent bonding fails to provide a real insight or explanation of bonding while the kinetic energy mechanism is both sound and accurate.

In a previous study, we introduced a generalized formulation of canonical transformations and spectra. These investigations explored the concept of a canonical potential strictly within the Born-Oppenheimer approximation for the most accurate available ground electronic state pairwise intermolecular potentials in H_2, HeH^+, and LiH [12]. Explicit canonically-based transformations have also been developed for transformation to a canonical potential for both these diatomics as well as two body intermolecular interactions [13,14]. The latter include several categories of bonding from van der Waals, hydrogen and halogen bonded

systems. The term canonical potential in these cases refers to a class of molecules with respect to a dimensionless function obtained from each molecule within the defined class by a readily invertible algebraic transformation. Furthermore, to be deemed canonical, the dimensionless potentials obtained from all of the molecules within the defined class by the canonical transformation must agree to within a specified order of accuracy. Now, a unified canonical approach to the molecular force, $F(R)$, in the systems H_2, HeH^+, and LiH is introduced based on H_2^+ as molecular reference. These transformations of $F(R)$ are demonstrated to be inherently canonical to high accuracy but the transformations have a distinctly different form from those corresponding to their respective Born-Oppenheimer potentials $E(R)$. To illustrate further applications of this methodology this approach is extended to systems with significantly different bonding characteristics. These will include Mg_2 [15], benzene dimer [16], and water dimer [17] considered within the radial limit. We shall, additionally, consider application of the developed force-based canonical approach to give insight into the electrostatic approach to chemical bonding initially advocated by Slater [10].

2. Methods

In constructing canonical representations of potentials for diatomic molecules [12,14], we developed an approach based upon a method for decomposing a 1-dimensional potential curve into a finite numbers of canonical sections that have the same scale invariant "shape" across a broad class of molecules. The notion of scale invariant shape utilized in this approach asserts that each designated section of the potential curve for one molecule has a unique counterpart in another molecule for which there exits an affine transformation to a single dimensionless curve.

Each such affine transformation is determined by the requirement that its endpoints map linearly to the endpoints of the single dimensionless "canonical" curve.

The key to identifying the counterpart sections of two given dimensional potentials was found to lie with their associated force distributions. More specifically, the 1-dimensional potential $E(R)$ has an associated force distribution $F(R) := -E'(R)$. For a given diatomic potential, R_e denotes its equilibrium separation, with $F(R_e) = 0$ (See Figure 1) and $E(R_e) = -D_e$ is the depth of the potential well. Also, the "maximum attractive" force F_m was defined by $F_m := \max_{R > R_e} |F(R)|$. In additional for $R > R_m$, the sequence of separation distances $R_m < R_{aj}, j = 1, 2, \ldots$, was defined by $|F(R_{aj})| = F_m 2^{-j}$ where R_{a1} is the separation distance at which the attractive force has been reduced to half its maximum value, etc. Correspondingly, for $R < R_e$, the sequence $R_{rj}, j = 0, 1, \ldots$, is defined by $F(R_{rj}) = F_m 2^j$ where R_{r0} is the separation distance at which the repulsive force equals the magnitude of the largest attractive force, etc. It was observed previously [12,14] that for given j, sections of the potential curves for two different molecules in the considered classes defined by $R_{a(j-1)} < R < R_{aj}$ or $R_{rj} < R < R_{r(j-1)}$ are canonical. Thus, identifying the canonical nature of the potentials for the considered classes of molecules rests fundamentally upon the associated force distributions. In the present contribution, this intrinsic connection between the canonical nature of molecular potentials and their associated force distributions is deepened by demonstrating that the force distributions are themselves canonical.

The sequences R_{aj} and R_{rj} defined above for identifying canonical segments of potential curves can initially be generalized. Specifically, given $1 < \alpha$, the sequence $R_m < R_{aj}(\alpha), j = 1, 2, \ldots$, can be defined by $|F(R_{aj}(\alpha))| = F_m \alpha^{-j}$. For $R < R_m$, the sequence R_{rj} above must be modified to

$R_{rj}(\alpha)$, $j = 1, 2, \ldots$, and defined by $F(R_{rj}(\alpha)) = F_m(\alpha^j - 2)$. Clearly, the original sequences R_{aj} and R_{rj} correspond to $\alpha = 2$. Also, for all $\alpha > 1$, it is implicit that $R_{r0}(\alpha) = R_{a0}(\alpha) = R_m$.

For $\alpha > 2$, the sequences $R_{aj}(\alpha)$ and $R_{rj}(\alpha)$ are less dense on the interval $0 < R$ while for $1 < \alpha < 2$, the sequences are more dense. The choice of α is thus guided by the required accuracy of a canonical representation of a given potential for an intended application. For example, it was shown in Ref. [12] that by appealing to both the piecewise affine transformation to canonical form and its inverse, one can construct a representation of the potential for any molecule in the considered class in terms of the potential for one of the molecules chosen as reference. In Ref. [12] this was taken to be H_2^+ the simplest molecular system. These canonical representations for each molecule in the considered class where then substituted into the Schrödinger equation to compute an approximations to its energy spectrum. This use of the canonical representation of a potential required considerable accuracy. Other applications of these canonical potential representations might be less demanding on accuracy.

2.1. Canonical Force Distribution

This section begins with introducing a simple dimensionless force distribution obtained from its dimensional counterpart $F(R)$ by a piecewise affine transformation. Subsequently, a somewhat more general piecewise affine transformation and associated dimensionless form are introduced that more accurately identifies canonical sections of force curves. These transformations to dimensionless form treat the attractive $(R > R_m)$ and repulsive $(0 < R < R_m)$ sides of the dimensional force curves separately.

2.2. Piecewise Affine Transformation to Canonical Dimensionless Form

For $j = 1, 2, \ldots$, define the dimensionless (attractive) force distribution $\tilde{F}_{aj}(x;\alpha)$ for $0 \leq x \leq 1$ by:

$$\tilde{F}_{aj}(x;\alpha) := \frac{F_s(xR_{aj}(\alpha)+(1-x)R_{a(j-1)}(\alpha))\alpha^j + \alpha}{(\alpha-1)}, \tag{1}$$

where

$$F_s(R) := \frac{F(R)}{F_m} \tag{2}$$

is the force distribution scaled by its maximum attractive value and

$$x = \frac{R - R_{a(j-1)}(\alpha)}{R_{aj}(\alpha) - R_{a(j-1)}} \quad \text{for} \quad R_{a(j-1)}(\alpha) < R < R_{aj}(\alpha). \tag{3}$$

Correspondingly, one can define the dimensionless (repulsive) force distribution $\tilde{F}_{rj}(x;\alpha)$

for $0 \leq x \leq 1$ by:

$$\tilde{F}_{rj}(x;\alpha) := \frac{(F_s(xR_{rj}(\alpha)+(1-x)R_{r(j-1)}(\alpha))+2)\alpha^{1-j} - 1}{(\alpha-1)} \tag{4}$$

with

$$x = \frac{R - R_{r(j-1)}(\alpha)}{R_{rj}(\alpha) - R_{r(j-1)}} \quad \text{for} \quad R_{rj}(\alpha) < R < R_{r(j-1)}(\alpha). \tag{5}$$

2.3. Inverse Canonical Transformation

The affine transformations in Eqs. (1) and (4) are readily inverted by the formulas:

$$\alpha^j F_s(R) = (\alpha-1)\tilde{F}_{aj}(x;\alpha) - \alpha \quad \text{for} \quad R_{a(j-1)}(\alpha) < R < R_{aj}(\alpha) \tag{6}$$

and x given by Eq. (3), and

$$\alpha^{1-j}(F_s(R)+2) = 1 + (\alpha-1)\tilde{F}_{rj}(x;\alpha) \quad \text{for} \quad R_{rj}(\alpha) < R < R_{r(j-1)}(\alpha) \tag{7}$$

with x given by Eq. (5).

The dimensionless forms Eqs. (1) and (4) are called canonical relative to a given class of

molecules if they agree up to a specified order of accuracy for every molecule in the given class.

It follows that by choosing one molecule in the given class as reference, then the force

distribution for every other molecule in the class can be approximated to a specified order of accuracy by a piecewise affine scaling of the reference force distribution. More specifically, let $F^*(R^*)$ denote the reference force distribution and $F(R)$ the force distribution for any other molecule in the given class. Appealing to Eqs. (1), (6), (4), and (7) one concludes that:

$$F_s(R) = F_s^*(R^*),$$ (8)

where

$$R^* = \begin{cases} R_{a(j-1)}^*(\alpha) + \left(\dfrac{R_{aj}^*(\alpha) - R_{a(j-1)}^*(\alpha)}{R_{aj}(\alpha) - R_{a(j-1)}(\alpha)} \right)\left(R - R_{a(j-1)}(\alpha)\right), & R_{a(j-1)}(\alpha) < R < R_{aj}(\alpha) \\[4mm] R_{r(j-1)}^*(\alpha) + \left(\dfrac{R_{rj}^*(\alpha) - R_{r(j-1)}^*(\alpha)}{R_{rj}(\alpha) - R_{r(j-1)}(\alpha)} \right)\left(R - R_{r(j-1)}(\alpha)\right), & R_{rj}(\alpha) < R < R_{r(j-1)}(\alpha) \end{cases}$$ (9)

and hence that:

$$F(R) = \frac{F_m}{F_m^*} F^*(R^*).$$ (10)

2.4. Generalized Canonical Transformation

As stated above, it proves helpful to generalize Eqs. (1) – (10) to more accurately identify canonical segments of force curves for molecules in the given class. Specifically, having chosen one molecule in the given class as reference, a sequence of generalized canonical forms $\tilde{F}_{aj}(x;\alpha;\gamma_j)$ and $\tilde{F}_{rj}(x;\alpha;\gamma_j)$, $j = 1, 2, \ldots$, can be defined as follows.

$$\tilde{F}_{a1}(x;\alpha;\gamma_1) := \frac{F_s(xR_{a1}(\alpha;\gamma_1) + (1-x)R_m) + 1}{F_s(R_{a1}(\alpha;\gamma_1)) + 1}$$ (11)

$$\tilde{F}_{r1}(x;\alpha;\gamma_1) := \frac{F_s(xR_{r1}(\alpha;\gamma_1) + (1-x)R_m) + 1}{F_s(R_{r1}(\alpha;\gamma_1)) + 1},$$ (12)

where

$$R_{a1}(\alpha;\gamma_1) := \gamma_1 R_{a1}(\alpha) + (1-\gamma_1)R_m$$ (13)

$$R_{\mathrm{r1}}(\alpha;\gamma_1) := \gamma_1 R_{\mathrm{r1}}(\alpha) + (1-\gamma_1)R_{\mathrm{m}} \tag{14}$$

and with γ_1 chosen to satisfy:

$$\begin{cases} \tilde{F}_{\mathrm{a1}}(0.5;\alpha;\gamma_1) = \tilde{F}_{\mathrm{a1}}^*(0.5;\alpha) & \text{for} \quad R > R_{\mathrm{m}} \\ \tilde{F}_{\mathrm{r1}}(0.5;\alpha;\gamma_1) = \tilde{F}_{\mathrm{r1}}^*(0.5;\alpha) & \text{for} \quad R < R_{\mathrm{m}} \end{cases}. \tag{15}$$

For $j = 2, 3, \ldots$, $\tilde{F}_{\mathrm{a}j}(x;\alpha;\gamma_j)$ and $\tilde{F}_{\mathrm{r}j}(x;\alpha;\gamma_j)$ are defined inductively through:

$$\tilde{F}_{\mathrm{a}j}(x;\alpha;\gamma_j) := \frac{F_s(xR_{\mathrm{a}j}(\alpha;\gamma_j) + (1-x)R_{\mathrm{a}(j-1)}(\alpha;\gamma_{j-1})) - F_s(R_{\mathrm{a}(j-1)}(\alpha;\gamma_{j-1}))}{F_s(R_{\mathrm{a}j}(\alpha;\gamma_j)) - F_s(R_{\mathrm{a}(j-1)}(\alpha;\gamma_{j-1}))} \tag{16}$$

$$\tilde{F}_{\mathrm{r}j}(x;\alpha;\gamma_j) := \frac{F_s(xR_{\mathrm{r}j}(\alpha;\gamma_j) + (1-x)R_{\mathrm{r}(j-1)}(\alpha;\gamma_{j-1})) - F_s(R_{\mathrm{r}(j-1)}(\alpha;\gamma_{j-1}))}{F_s(R_{\mathrm{r}j}(\alpha;\gamma_j)) - F_s(R_{\mathrm{r}(j-1)}(\alpha;\gamma_{j-1}))} \tag{17}$$

where γ_j is chosen to satisfy:

$$\begin{cases} \tilde{F}_{\mathrm{a}j}(0.5;\alpha;\gamma_j) = \tilde{F}_{\mathrm{a}j}^*(0.5;\alpha) & \text{for} \quad R > R_{\mathrm{m}} \\ \tilde{F}_{\mathrm{r}j}(0.5;\alpha;\gamma_j) = \tilde{F}_{\mathrm{r}j}^*(0.5;\alpha) & \text{for} \quad R < R_{\mathrm{m}} \end{cases} \tag{18}$$

with

$$R_{\mathrm{a}j}(\alpha;\gamma_j) := \gamma_j R_{\mathrm{a}j}(\alpha) + (1-\gamma_j)R_{\mathrm{a}(j-1)}(\alpha;\gamma_{j-1}) \tag{19}$$

$$R_{\mathrm{r}j}(\alpha;\gamma_j) := \gamma_j R_{\mathrm{r}j}(\alpha) + (1-\gamma_j)R_{\mathrm{r}(j-1)}(\alpha;\gamma_{j-1}). \tag{20}$$

For this generalized canonical form to be considered canonical, $\tilde{F}_{\mathrm{a}j}(x;\alpha;\gamma_j)$ and $\tilde{F}_{\mathrm{r}j}(x;\alpha;\gamma_j)$ must agree with the reference forms $\tilde{F}_{\mathrm{a}j}^*(x;\alpha)$ and $\tilde{F}_{\mathrm{r}j}^*(x;\alpha)$, respectively, to a desired degree of accuracy, as is demonstrated below for the considered class of molecules in which H_2^+ is taken as reference. It follows that for each j, the portions of the force curves $F(R)$ for $R_{\mathrm{a}(j-1)}(\alpha;\gamma_{j-1}) < R < R_{\mathrm{a}j}(\alpha;\gamma_j)$ and $F^*(R^*)$ for $R_{\mathrm{a}(j-1)}^*(\alpha) < R^* < R_{\mathrm{a}j}^*(\alpha)$ have the "same shape" in that one can write $F(R)$ as a simple affine scaling of $F^*(R^*)$. In particular, from Eq. (11), one can write for $R_{\mathrm{m}} < R < R_{\mathrm{a1}}(\alpha;\gamma_1)$

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$$F_s(R) = \frac{\alpha}{\alpha-1}(1 + F_s(R_{a1}(\alpha;\gamma_1)))\left[1 + F_s^*\left(R_m^* + \frac{(R_{a1}^* - R_m^*)}{(R_{a1}(\alpha;\gamma_1) - R_m)}(R - R_m)\right)\right] - 1 . \qquad (21)$$

Similarly, from Eq. (12), one has fore $R_{r1}(\alpha;\gamma_1) < R < R_m$

$$F_s(R) = \frac{(1 + F_s(R_{r1}(\alpha;\gamma_1)))}{(\alpha-1)}\left[1 + F_s^*\left(R_m^* + \frac{(R_{r1}^* - R_m^*)}{(R_{r1}(\alpha;\gamma_1) - R_m)}(R - R_m)\right)\right] - 1 . \qquad (22)$$

In the next section, these results are illustrated by taking $F(R)$ to be the force distribution for the target molecules (H_2, HeH^+, LiH, Mg_2, benzene dimer, and water dimer) and $F^*(R^*)$ to be the force distribution of the reference molecule, H_2^+.

3. Results

As discussed above, the key requirements for the dimensionless force distribution are given by Eqs. (11) and (12). A prescribed degree of accuracy across the class of molecules is also required for the dimensionless force to be considered canonical. Figure 2 is a plot of Eqs. (11) and (12) for the reference molecule H_2^+ and the target molecules H_2, HeH^+, and LiH. These four molecules were previously studied [12] in which it was demonstrated that their potentials had a dimensionless canonical form. Similarly, Fig. 3 is a plot of (11) and (12) for H_2^+, water dimer, benzene dimer, and magnesium dimer. More precisely, Table I gives the relative errors of this agreement between the dimensionless force distribution Eqs. (11) and (12) of the reference molecule H_2^+ and the other indicated molecules, where the Relative Error between two functions $f_1(x)$ and $f_2(x)$ over the interval $a \le x \le b$ is defined by:

$$\text{Relative Error} := \frac{\displaystyle\int_a^b |f_1(x) - f_2(x)| \, dx}{\displaystyle\int_a^b |f_1(x)| \, dx} . \qquad (23)$$

To illustrate applications of the formulas in Eqs. (21) and (22), Fig. 4 gives plots of the force distribution for the water dimer and its approximation using the H_2^+ reference force distribution. The relative error between these two force distribution curves is 0.0015.

4. Discussion

Initially, the concept of canonical potential was introduced to give a unified perspective on a range of ground state electronic potentials in diatomic molecules from CO, H_2^+, H_2, HF, LiH, Li_2, O_2, and Ar_2 and one-dimensional intermolecular cuts through the potentials of OC-HBr, OC-HF, OC-HCCH, OC-HCN, OC-HCl, OC-HI, OC-BrCl and OC-Cl_2. The ground state dissociation energies D_e ranged, over almost three orders of magnitude from 99.3 cm^{-1} to 90683 cm^{-1} and involved a wide range of different categories of chemical bonds from ionic to covalent to van der Waals, hydrogen bonded and halogen bonded pairwise interactions [13]. In subsequent studies this canonical approach was developed further generalized and improved [12,14] and its accuracy tested to high level within the Born-Oppenheimer approximation for molecules with few electrons. In the current studies, we have addressed the question as to whether canonical applications can be developed from the perspective of force with the versatility and accuracy corresponding to those already developed for canonical transformations and applications involving potentials. Although force is generically defined with respect to the negative of the derivative of potential, there is no expectation that their canonical transformations are necessarily the same and indeed this is found to be so. Figure 2 illustrates the dimensionless canonical force distributions for H_2^+ (solid curve), H_2 (red circles), HeH^+ (blue squares) and LiH (green diamonds). The dimensionless canonical force distribution for H_2^+ (solid curve) vs water dimer (red circles), benzene dimer (blue squares) and Mg_2 (green diamonds) for $j = 1$ and $\alpha = 2$

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are also shown in Figure 3. These figures demonstrate clearly the ability of the proposed

canonical approach to transform the force distribution of a wide range of prototypical species in

different chemical bonding categories to a single dimensionless form. In each case, the

transformed dimensionless force distributions of the selected prototypical systems can be

superimposed on the corresponding dimensionless force distribution of the selected reference

molecule H_2^+, the simplest molecule. Relative errors between the dimensionless canonical force

distribution for this reference H_2^+ and those for HeH^+, H_2, LiH, Mg_2, water dimer and benzene

dimer for $\alpha = 2$ are shown in Table 1. These results demonstrate that canonical transformations

do exist for force within a maximum relative error of < 0.008. The estimated errors can be

compared with results for transformations in the corresponding potentials that have been

calculated in the case of certain of the prototype molecules studied. The corresponding relative

errors are approximately a factor of two smaller, probably a consequence of the greater difficulty

in determining force information relative to that corresponding to potential.

The generation of accurate intermolecular interactions potentials, and thus forces, of

water is a theoretical and computational challenging problem. Recent works have produced

accurate potentials for water dimer [17-19], water trimer [20,21], and many body water

interactions [20-22] exploiting the limits of current theoretical methods computational

capabilities. Figure 4 shows the radial force distribution of water dimer generated from H_2^+.

Comparing with the true force distribution [17], the relative error is 0.0015. Taking in

consideration the simplicity of the canonical approach in terms of computational cost, these

results can be view as a truly remarkable. Efforts are underway to extend this canonical approach

to other degree of freedom in water dimer.

Now that we have developed and demonstrated semi-empirically that canonical

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applications involving force do exist, questions arise as to whether they can give insight into the fundamental nature of chemical bonding and in particular into the electrostatic model. It is recognized that the developed procedures have implications with respect to the fundamental origins of chemical bonding that go back to the initial conceptualization and developments of such bonding [1-11]. The electrostatic model of chemical bonding, in particular, at a fundamental level is force-based as emphasized in the original work of Feynman [3]. Detailed consideration of the basis of this perspective has been extensively reviewed through application of the Hellmann-Feynman and Virial theorems for diatomic molecules by Bader [11]. The latter considered the variation of V (electronic potential) and T (electronic kinetic energy) with internuclear distance R leading to the criterion that it is the minimization of the potential energy correlated with maximization of electron density between the nuclei that determines binding energy. The additional availability of very accurate potentials for H_2^+, H_2, HeH^+, and LiH [12] within the Born-Oppenheimer approximation and the developed canonical approaches to potential and force have now provided an avenue of investigating the fundamental nature of this electrostatic model of bonding from a totally different perspective. The latter will require an additional investigation of the canonical behavior of electronic kinetic energy $T(R)$, the quantity $RF(R)$ in addition to the canonical dependence of $V(R)$ and $F(R)$. Such investigations are currently underway and will be the subject of future publications.

Concerning the canonical nature of both the potential $E(R)$ and its associated force $F(R)$ that has been demonstrated for the considered class of molecules, there is a strong argument for viewing the canonical nature of the force as the more fundamental notion. Indeed, having demonstrated that the force is canonical for a given class of molecules, it follows immediately that the associated potential must also be canonical (see Appendix A for proof), whereas, the

reverse implication is false in general. That is, the potentials for a given class of molecules can be canonical, as defined above, without immediately implying that their associated force distributions are also canonical. That must be demonstrated through a separate analysis.

5. Conclusions

In previous investigations, we have demonstrated that the concept of canonical potentials could give a unified perspective on a wide categories of chemical bonding from ionic to covalent molecules as well as weakly bound including van der Waals, hydrogen and halogen bonded intermolecular interactions. From the fundamental perspective of the Hellmann-Feynman Theorem, corresponding canonical studies have now been promulgated through consideration of force. From such canonical perspectives, we have now demonstrated that for a prototype group of molecules (H_2^+, H_2, HeH^+, and LiH for which extremely accurate potentials within the Born-Oppenheimer exist), it has been possible to determine accurate force distributions and demonstrate their canonical nature. Furthermore, we have now extended such analyses to molecular species with different bonding characteristics including Mg_2 and the radial analyses of benzene and water dimer. The canonical force approach developed is thus demonstrated to be equally applicable in these cases. The latter prototypical systems have great significant in modeling molecular aggregation of magnesium, π-stacking interactions in structural biology, and the fundamental properties water in all phases of matter. The developed canonical force application should be ubiquitous and have other widespread applications in molecular modeling.

The reported results will be essential in subsequent applications that will require an additional investigation of the canonical behavior. These will included the electronic kinetic energy $T(R)$, the quantity $RF(R)$ in addition to the canonical dependence of $V(R)$ and $F(R)$ and other applications to chemical bonding through study of the Virial and Hellmann-Feynman

theorems. Such investigations are currently underway and will be the subject of future publications.

Acknowledgments

Appendix A: Canonical Force Implies Canonical Potential

In this appendix, it is shown that if for a given class of molecules, it has been shown that their force distributions are canonical in the sense discussed above, then their associated potentials must also be canonical. The proof of this assertion is given for the attractive side of the simplified canonical dimensionless form presented in Section 2.2. The proofs for the repulsive side of the simplified form and for the more general canonical form presented in Section 2.4 are similar and hence omitted.

Let $E(R)$ and $F(R) = -E'(R)$ denote the potential and associated force distribution for a generic molecule in the chosen class, and let $E^*(R)$ and $E^{*'}(R)$ denote the reference potential and force. Consider the dimensionless force distribution for $F(R)$ given by Eqs. (1) – (3), and for the reference molecule by:

$$\tilde{F}_{aj}^*(x;\alpha) := \frac{F_s^*(xR_{aj}^*(\alpha) + (1-x)R_{a(j-1)}^*(\alpha))\alpha^j + \alpha}{(\alpha-1)} \, , \tag{A1}$$

where

$$F_s^*(R^*) := \frac{F^*(R^*)}{F_m^*} \tag{A2}$$

is the reference force distribution scaled by its maximum attractive value and

$$x = \frac{R^* - R_{a(j-1)}^*(\alpha)}{R_{aj}^*(\alpha) - R_{a(j-1)}^*} \quad \text{for} \quad R_{a(j-1)}^*(\alpha) < R^* < R_{aj}^*(\alpha). \tag{A3}$$

Force is considered canonical if

$$\tilde{F}_{aj}(x;\alpha) \approx \tilde{F}_{aj}^*(x;\alpha) \tag{A4}$$

for all molecules within the chosen class with

$$\frac{R - R_{\mathrm{r}(j-1)}(\alpha)}{R_{\mathrm{r}j}(\alpha) - R_{\mathrm{r}(j-1)}(\alpha)} = x = \frac{R^* - R^*_{\mathrm{a}(j-1)}(\alpha)}{R^*_{\mathrm{a}j}(\alpha) - R^*_{\mathrm{a}(j-1)}(\alpha)} \tag{A5}$$

for

$$R_{\mathrm{a}j}(\alpha) < R < R_{\mathrm{a}(j-1)}(\alpha) \quad \text{and} \quad R^*_{\mathrm{a}(j-1)}(\alpha) < R^* < R^*_{\mathrm{a}j}(\alpha). \tag{A6}$$

More precisely, Eq. (A4) requires that:

$$| \tilde{F}_{\mathrm{a}j}(x;\alpha) - \tilde{F}^*_{\mathrm{a}j}(x;\alpha) | \; < \; \epsilon \quad \text{for} \quad 0 \le x \le 1, \tag{A7}$$

where $0 < \epsilon \ll 1$ is a specified error tolerance. Also, from Eq. (A5), one sees that:

$$
\begin{aligned}
R^* = \lambda_j[R] &:= R^*_{\mathrm{a}(j-1)}(\alpha) + \frac{(R^*_{\mathrm{a}j}(\alpha) - R^*_{\mathrm{a}(j-1)}(\alpha))}{(R_{\mathrm{a}j}(\alpha) - R_{\mathrm{a}(j-1)}(\alpha))}(R - R_{\mathrm{a}(j-1)}(\alpha)) \\
&= R^*_{\mathrm{a}(j-1)}(\alpha) + \dot{\lambda}_j(R - R_{\mathrm{a}(j-1)}(\alpha)).
\end{aligned}
\tag{A8}
$$

Notice that $\lambda_j[R]$ is an affine mapping (that is, $\lambda'_j[R] = \dot{\lambda}_j$ where $\dot{\lambda}_j$ is a constant) of the

interval $R_{\mathrm{a}(j-1)}(\alpha) < R < R_{\mathrm{a}}(\alpha)$ onto the interval $R^*_{\mathrm{a}(j-1)}(\alpha) < R^* < R^*_{\mathrm{a}j}(\alpha)$.

Appealing to the inverse canonical transformation in Eq. (6), it follows that:

$$F_s(R)\alpha^j + \alpha = (\alpha - 1)\tilde{F}_{\mathrm{a}j}(x;\alpha) \approx (\alpha - 1)\tilde{F}^*_{\mathrm{a}j}(x;\alpha) = F^*_s(R^*)\alpha^j + \alpha \tag{A9}$$

from which it follows that:

$$F_s(R) \approx F^*_s(R^*) = F^*_s(\lambda_j[R]) \quad \text{for} \quad R_{\mathrm{a}(j-1)}(\alpha) < R < R_{\mathrm{a}j}(\alpha) \tag{A10}$$

or more precisely that:

$$| F_s(R) - F^*_s(\lambda_j[R]) | \; < \; \epsilon \quad \text{for} \quad R_{\mathrm{a}(j-1)}(\alpha) < R < R_{\mathrm{a}j}(\alpha). \tag{A11}$$

Now, define the scaled potentials $E_s(R) := E(R) / F_{\mathrm{m}}$ and $E^*_s(R^*) := E^*(R^*) / F^*_{\mathrm{m}}$.

Then one concludes that for $R_{\mathrm{a}(j-1)}(\alpha) < R < R_{\mathrm{a}j}(\alpha)$:

$$E_s(R_{a(j-1)}(\alpha)) - E_s(R) = \int_{R_{a(j-1)}(\alpha)}^{R} F_s(r)dr$$

$$\approx \int_{R_{a(j-1)}(\alpha)}^{R} F_s^*(\lambda_j[r])dr$$

$$= \frac{1}{\lambda_j} \int_{\lambda_j[R_{a(j-1)}(\alpha)]}^{\lambda_j[R]} F_s^*(\rho)d\rho \qquad (A12)$$

$$= \frac{1}{\lambda_j} \int_{[R_{a(j-1)}^*(\alpha)]}^{\lambda_j[R]} F_s^*(\rho)d\rho$$

$$= \frac{1}{\lambda_j} (E_s^*(R_{a(j-1)}^*(\alpha)) - E_s^*(\lambda_j[R])).$$

From Eq. (A12), it follows that:

$$|E_s(R) - A[E_s^*(\lambda_j[R])]| \leq \int_{R_{a(j-1)}(\alpha)}^{R} |F_s(r) - F_s^*(\lambda_j[r])| \, dr$$

$$< (R_{aj}(\alpha) - R_{a(j-1)}(\alpha))\epsilon(\alpha-1) \qquad (A13)$$

with the affine transformation $A[\cdot]$ defined by:

$$A[E_s^*(\lambda_j[R])] := \frac{E_s^*(\lambda_j[R]) - E_s^*(R_{a(j-1)}^*(\alpha))}{\lambda_j} - E_s(R_{a(j-1)}(\alpha)). \qquad (A14)$$

Thus, from Eq. (A13), one sees that up to a specified order of approximation, the scaled potential

$E_s(R)$ is equivalent to an affine transformation of the scaled reference potential $E_s^*(\lambda_j[R])$.

Hence $E(R)$ for $R_{a(j-1)}(\alpha) < R < R_{aj}(\alpha)$ and $E^*(R^*)$ for $R_{a(j-1)}^*(\alpha) < R^* < R_{aj}^*(\alpha)$ have, up to the

specified order of error, the same canonical form in the sense define above.

Next consider the generalized canonical transformation and its inverse of Section 2.4

given by formulas Eqs. (11) – (22). Corresponding to Eqs. (A4) – (A6) one shows that:

$$\tilde{F}_{aj}(x;\alpha;\gamma_j) \approx \tilde{F}_{aj}^*(x;\alpha) \qquad (A15)$$

for all molecules within the chosen class with

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$$\frac{R - R_{a(j-1)}(\alpha)}{R_{aj}(\alpha;\gamma_j) - R_{a(j-1)}(\alpha)} = x = \frac{R^* - R^*_{a(j-1)}(\alpha)}{R^*_{aj}(\alpha) - R^*_{a(j-1)}(\alpha)} \tag{A16}$$

for

$$R_{a(j-1)}(\alpha) < R < R_{aj}(\alpha;\gamma_j) \quad \text{and} \quad R^*_{a(j-1)}(\alpha) < R^* < R^*_{aj}(\alpha). \tag{A17}$$

Then Eq. (A7) and (A8) take the form:

$$|\tilde{F}_{aj}(x;\alpha;\gamma_j) - \tilde{F}^*_{aj}(x;\alpha)| < \epsilon \quad \text{for} \quad 0 \le x \le 1 \tag{A18}$$

and

$$\begin{aligned} R^* = \lambda_j[R] &:= R^*_{a(j-1)}(\alpha) + \frac{(R^*_{aj}(\alpha) - R^*_{a(j-1)}(\alpha))}{(R_{aj}(\alpha;\gamma_j) - R_{a(j-1)}(\alpha))}(R - R_{a(j-1)}(\alpha)) \\ &= R^*_{a(j-1)}(\alpha) + \dot{\lambda}_j(R - R_{a(j-1)}(\alpha)), \end{aligned} \tag{A19}$$

where one notices now that $\lambda_j[R]$ is an affine mapping (that is, $\lambda'_j[R] = \dot{\lambda}_j$ where $\dot{\lambda}_j$ is a

constant) of the interval $R_{a(j-1)}(\alpha) < R < R_{aj}(\alpha;\gamma_j)$ onto the interval $R^*_{a(j-1)}(\alpha) < R^* < R^*_{aj}(\alpha)$. A

key observation is that:

$$F_s(R_{aj}(\alpha;\gamma_j))\alpha^j = 1 \quad \text{if and only if} \quad \gamma_j = 1. \tag{A20}$$

Since $R_{aj}(\alpha;1) = R_{aj}(\alpha)$ and $R_{aj}(\alpha)$ is chosen to satisfy Eq. (A20). Following a rather

lengthy calculation similar to that leading to Eq. (A12), one can show that Eqs. (A13) and (A14)

generalize to:

$$\begin{aligned} |E_s(R) - A[E^*_s(\lambda_j[R])]| &< (R_{aj}(\alpha;\gamma_j) - R_{a(j-1)}(\alpha))\Big(|F_s(R_{aj}(\alpha;\gamma_j)\alpha^j + \alpha|\epsilon \\ &+ \alpha\left|1 - \frac{F_s(R_{aj}(\alpha;\gamma_j))\alpha^j + \alpha}{\alpha - 1}\right| \Big) \end{aligned} \tag{A21}$$

and

$$A[E_s^*(\lambda_j[R])] := \left(\frac{E_s^*(\lambda_j[R]) - E_s^*(R_{a(j-1)}^*(\alpha))}{\lambda_j} \right) \left(\frac{F_s(R_{aj}(\alpha;\gamma_j))\alpha^j + \alpha}{\alpha - 1} \right) \tag{A22}$$
$$- E_s(R_{a(j-1)}(\alpha)).$$

It is not difficult to show that Eqs. (A21) and (A22) reduce to Eqs. (A13) and (A14) when $\gamma_j = 1$

because $F_s(R_{aj}(\alpha;\gamma_j))\alpha^j \to -1$ as $\gamma_j \to 1$. It is important to notice that the order of accuracy in

the approximation of $E_s(R)$ by $A[E_s^*(\lambda_j[R])]$ depends upon both ϵ, the order of error in the

canonical force approximation, and also the second term in Eq. (A21). The second term in Eq.

(A21) can be made small by γ_j being near 1 and by taking α near 1. It is important to recognize

that the value of γ_j used here is chosen to satisfy Eq. (18), that is, $\tilde{F}_{aj}(0.5;\alpha;\gamma_j) = \tilde{F}_{aj}^*(0.5;\alpha)$. If

one constructs the canonical potential directly, that is, not from the canonical force distribution

as done in this appendix, then γ_j is chosen to satisfy

$$\tilde{E}_{aj}(0.5;\alpha;\gamma_j) = \tilde{E}_{aj}^*(0.5;\alpha). \tag{A23}$$

In general, these two values of γ_j will not be the same, though the difference will not be great.

However, the error in the approximation of $\tilde{E}_{aj}(x;\alpha;\gamma_j)$ by $\tilde{E}_{aj}^*(0.5;\alpha)$ for $0 \le x \le 1$ will be

smaller when γ_j is chosen according to Eq. (A23) rather than by Eq. (18).

Table I

Relative errors between the dimensionless canonical force distribution for the reference molecule H_2^+ and those for HeH^+, H_2, LiH, Mg_2, water dimer, and benzene dimer for $\alpha = 2$.

Molecule	$R_{a0} - R_{a1}$	$R_{a1} - R_{a2}$	$R_{r1} - R_{r0}$	$R_{r2} - R_{r1}$
H_2	0.00254	0.00133	0.0061	0.000588
HeH^+	0.00419	0.000422	0.00131	0.0015
LiH	0.00805	0.00477	0.0016	0.000746
Benzene Dimer	0.00322	0.00112	0.00721	0.0025
Water Dimer	0.00101	0.00114	0.00493	0.00179
Mg_2	0.00589	0.00617	0.00674	0.00153
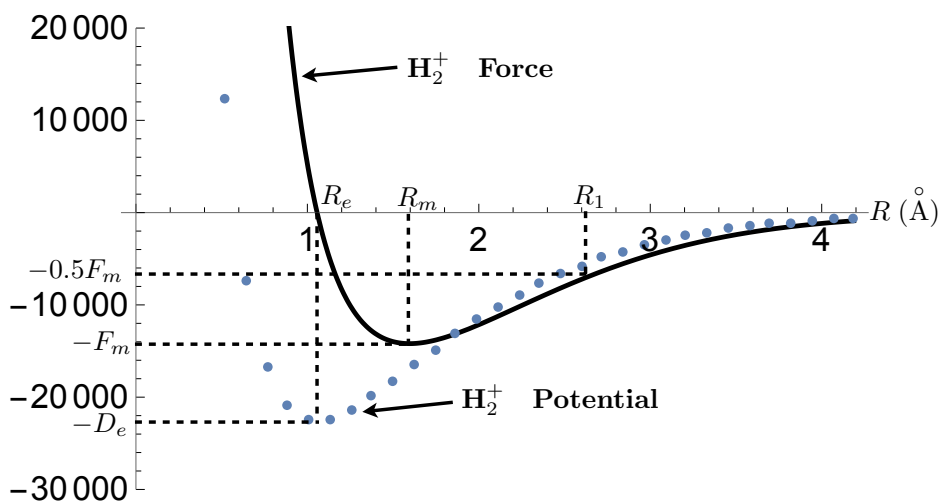
Figure 1. The potential, $E(R)$, (dotted curve) and force distribution, $F(R)$, (solid curve) for the reference molecule H_2^+.
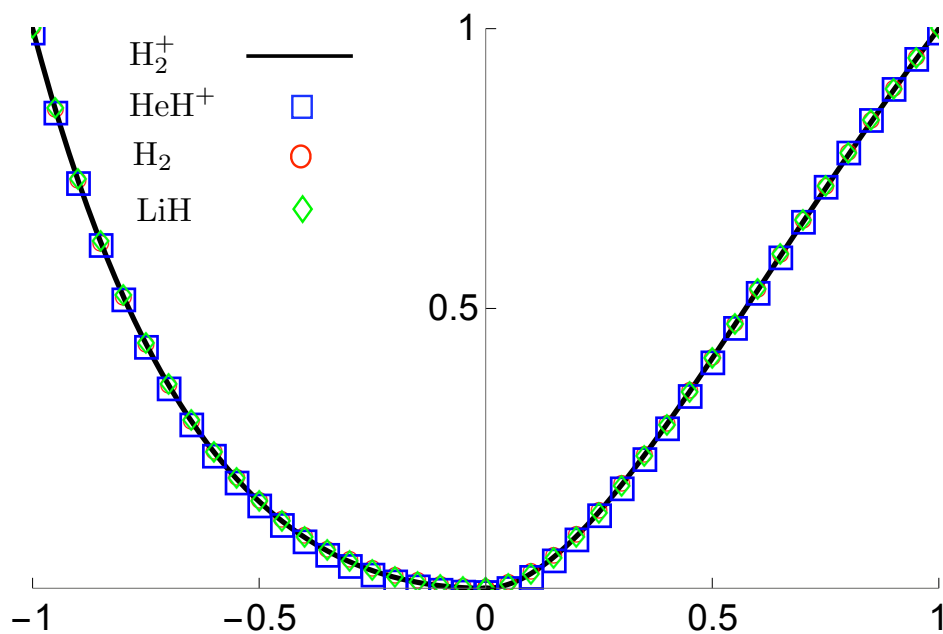
Figure 2. Dimensionless canonical force distributions for H_2^+ (solid curve), H_2 (red circles), HeH^+ (blue squares) and LiH (green diamonds).
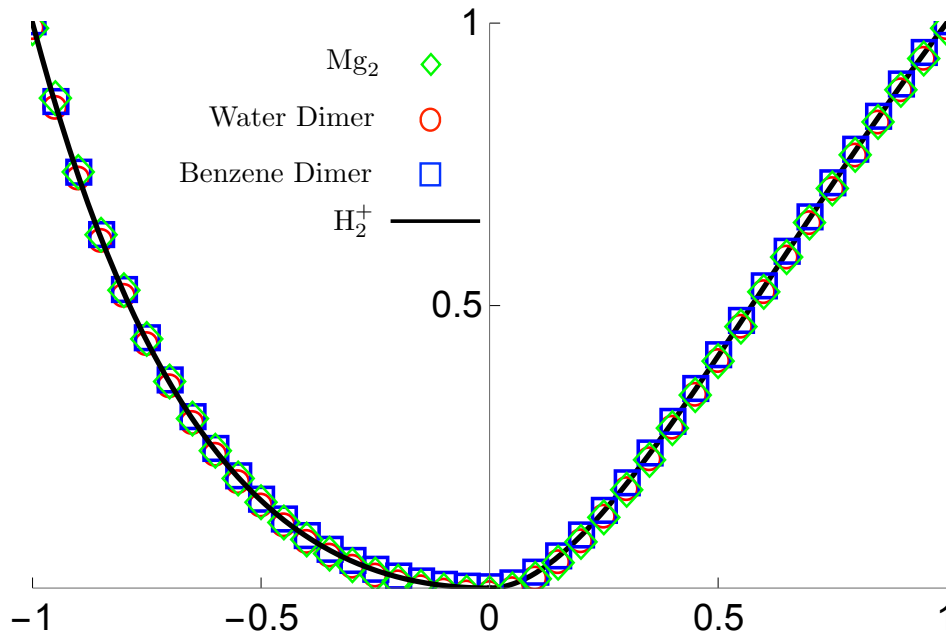

Figure 3. Dimensionless canonical force distribution for H_2^+ (solid curve) vs water dimer (red circles), benzene dimer (blue squares) and Mg_2 (green diamonds) for $j = 1$ and $\alpha = 2$.
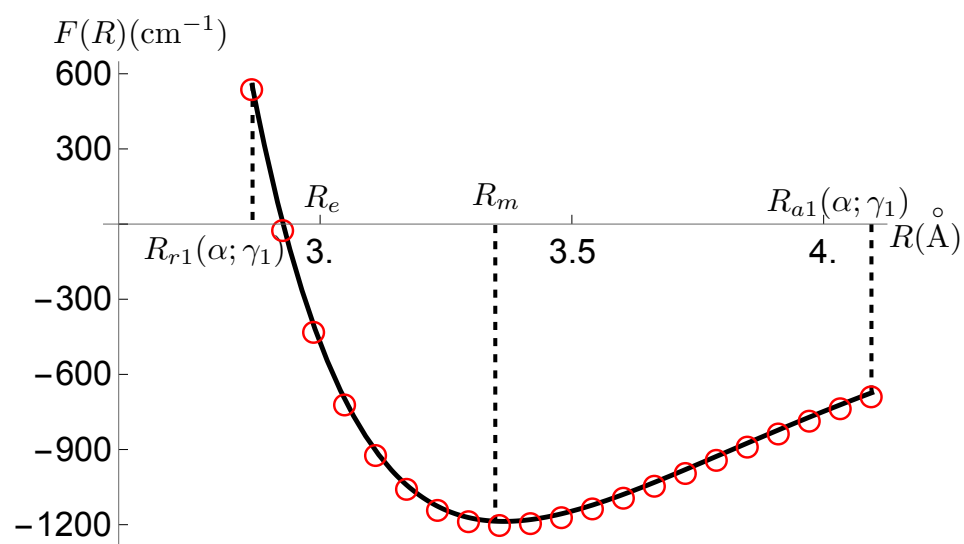
Figure 4. True force distribution for water dimer (solid curve) vs. approximation using force distribution for H_2^+ (red circles) with $\alpha = 2$.

References

[1] I. M. Torrens, Intermolecular Potentials, Academic Press, New York, 1972, p 3.

[2] P. Needham, Studies in History and Philosophy of Science 45, 1 (2014).

[3] R. P. Feynman, Phys. Rev. 56, 340 (1939).

[4] B. M. Deb (Ed.), The force concept in chemistry, Van Nostrand Reinhold, New York, 1981.

[5] G. B. Bacskay and S. Nordholm, J. Phys. Chem. A. 117, 7946 (2013).

[6] H. Hellmann, Zeitschrift für Physik 85, 180 (1933).

[7] M. Feinberg and K. Ruedenberg, J. Chem. Phys. 54, 1495 (1971).

[8] M. Feinberg and K. Ruedenberg, J. Chem. Phys. 55, 5804 (1971).

[9] K. Ruedenberg and M. W. Schmidt, J. Phys. Chem. A 113, 1954 (2009).

[10] J. C. Slater, J. Chem. Phys. 1, 687 (1933).

[11] R. F. W. Bader, The Nature of Chemical Binding, in *The Force Concept in Chemistry*, edited by B. M. Deb (Van Nostrand Reinhold, New York, 1981), pp. 39-136.

[12] J. R. Walton, L. A. Rivera-Rivera, R. R. Lucchese, and J. W. Bevan, J. Phys. Chem. A 119, 6753 (2015). In this reference, the notation $V(R)$ corresponds to the notation $E(R)$ used in the current work.

[13] R. R. Lucchese, C. K. Rosales, L. A. Rivera-Rivera, B. A. McElmurry, J. W. Bevan, and J. R. Walton, J. Phys. Chem. A 118, 6287 (2014). In this reference, the notation $V(R)$ corresponds to the notation $E(R)$ used in the current work.

[14] J. R. Walton, L. A. Rivera-Rivera, R. R. Lucchese, and J. W. Bevan, Phys. Chem. Chem. Phys. 17, 14805 (2015).

[15] E. Czuchaj, M. Krosnicki, and H. Stoll, Theor. Chem. Acc. 107, 27 (2001).

[16] R. Podeszwa, R. Bukowski, and K. Szalewicz, J. Phys. Chem. A 110, 10345 (2006).

[17] A. Shank, Y. Wang, A. Kaledin, B. J. Braams, and J. M. Bowman, J. Chem. Phys. 130, 144314 (2009).

[18] V. Babin, C. Leforestier, and F. Paesani, J. Chem. Theory Comput. 9, 5395 (2013).

[19] P. Jankowski, G. Murdachaew, R. Bukowski, O. Akin-Ojo, C. Leforestier, and K. Szalewicz, J. Phys. Chem. A 119, 2940 (2015).

[20] U. Góra, W. Cencek, R. Podeszwa, A. van der Avoird, and K. Szalewicz, J. Chem. Phys.

140, 194101 (2014).

[21] V. Babin, G. R. Medders, and F. Paesani, J. Chem. Theory Comput. 10, 1599 (2014).

[22] G. R. Medders, A. W. Götz, M. A. Morales, P. Bajaj, and F. Paesani, 143, 104102 (2015).