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Title
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Abstract

Canonical approaches are applied for investigation of the electronic ground states of H_2^+, H_2, HeH^+, and LiH using the Virial Theorem. These approaches will be dependent on previous investigations involving the canonical nature of $E(R)$, the Born-Oppenheimer potential, and $F(R)$, the associated force of $E(R)$, that have been demonstrated to be individually canonical to high accuracy in the case of the systems investigated. Now, the canonical nature of the remaining functions in the Virial Theorem [the electronic kinetic energy $T(R)$, the electrostatic potential energy $V(R)$, and the function $W(R) = RF(R)$] are investigated and applied to H_2, HeH^+, and LiH with H_2^+ chosen as reference. The results will be discussed in the context of a different perspective of molecular bonding that goes beyond previous direct applications of the Virial Theorem.

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1. Introduction

Recently, the source of chemical bonding, particularly that involving the history and philosophy of covalent bonding, has been reviewed[1] and describes the diversity of approaches used to consider the fundamental physical basis of chemical bonding. This included the force-based concept of chemistry[2,3] 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,[4] the origin of bonding in the simplest molecule H_2^+ has been considered supporting a mechanism attributed to Hellmann[5] that lowering of kinetic energy and associated electron delocalization are considered as the sources for stabilization of the molecule and the key mechanism of bonding.[6-9] This conclusion was in contrast with the perspective of Slater,[10] Feynman,[2] Bader,[11,12] 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[4] 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.[13] 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. Explicit canonically-based transformations including a semi-empirically verified Rydberg-Klein-Rees approach to high accuracy, have also been developed for transformation to a canonical potential for both diatomics as well as two body intermolecular interactions.[14,15] 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, comprehensive canonical approaches are applied for investigation of the electronic ground states of H_2^+, H_2, HeH^+ and LiH using the Virial Theorem. In addition, the canonical nature of the electrostatic potential energy $V(R)$, the function $W(R)$ $=RF(R)$, and the electronic kinetic energy $T(R)$ that as a group proceed in precisely the same fashion, are now applied to H_2, HeH^+, and LiH with H_2^+ chosen as reference. These characteristic transformations together with the previously demonstrated[16] but different canonical nature of $E(R)$, the Born-Oppenheimer potential, and $F(R)$, the associated force of $E(R)$, are demonstrated to be inherently but individually canonical to high accuracy in the case of the systems investigated. The results will also be discussed in the context of giving a different perspective of molecular bonding that goes beyond previous direct applications of the Virial Theorem.

II. Methods

In Ref. 13 and 15, a method for constructing canonical representations of potentials for diatomic molecules was developed utilizing a scheme for decomposing a 1-dimensional potential curve into a finite numbers of canonical sections that have the same dimensionless "shape" across a broad class of molecules. The notion of dimensionless shape exploited in this approach is developed such that each designated section of the potential curve for one molecule has a unique counterpart in another molecule and an associated affine transformation that maps each corresponding section to a single dimensionless curve. Each affine transformation is determined

by the requirement that the endpoints of the section of the dimensional potential curve upon which it acts map linearly to the endpoints of a single dimensionless "canonical" curve.

Identifying the sections of two given dimensional potentials with the same canonical shape makes fundamental use of their associated force distributions (termed the "*Feynman Force*", *cf.* Ref. 2). More specifically, the 1-dimensional potential $E(R)$ is considered with associated force distribution

$$F(R) := -E'(R),$$
(1)

and R_e denotes the equilibrium separation distance, that is, the value of R at which the force is zero, for which $E(R_e) = -D_e$, the depth of the potential well. Also, the "maximum attractive force", F_m, is defined by $F_m := \max_{R > R_e} |F(R)|$ and its corresponding inter-nuclear separation distance $R_m > R_e$ for which $F(R_m) = F_m$. The subsequently defined sequence of separation distances $R_m < R_{aj}(\alpha), j = 1, 2, \ldots$ for which

$$|F(R_{aj}(\alpha))| = F_m / \alpha^j$$
(2)

where $\alpha > 1$ is a specified parameter. That is, $R_{a1}(\alpha)$ is the separation distance at which the attractive force has been reduced to α^{-1} times its maximum value, etc. Correspondingly, for $R < R_e$, the sequence $R_{rj}(\alpha), j = 0, 1, \ldots$ of separation distances is defined such that

$$|F(R_{rj}(\alpha))| = F_m \alpha^j.$$
(3)

Thus, $R_{r0}(\alpha)$ is the separation distance at which the repulsive force equals the magnitude of the largest attractive force, etc. It was shown in Ref. 13 and 15 that for given $j < k$, sections of the potential curves for two different molecules in the considered classes defined by $R_{aj}(\alpha) < R < R_{ak}(\alpha)$ or $R_{rk}(\alpha) < R < R_{rj}(\alpha)$ have canonical shapes. It was subsequently observed in Ref. 13 and

4

15 that enhanced accuracy in identifying corresponding sections of potential curves with canonical shapes results from generalizing Eqs. (2) and (3) to:

$$R_{a1}(\alpha;\gamma_1) := \gamma_1 R_{a1}(\alpha) + (1-\gamma_1)R_m(\alpha) \tag{4}$$

$$R_{aj}(\alpha;\gamma_j) := \gamma_j R_{aj}(\alpha) + (1-\gamma_j)R_{a(j-1)}(\alpha;\gamma_{j-1}), \quad j > 1 \tag{5}$$

$$R_{r1}(\alpha;\gamma_1) := \gamma_1 R_{r1}(\alpha) + (1-\gamma_1)R_{r0}(\alpha) \tag{6}$$

$$R_{rj}(\alpha;\gamma_j) := \gamma_j R_{aj}(\alpha) + (1-\gamma_j)R_{a(j-1)}(\alpha;\gamma_{j-1}), \quad j > 1. \tag{7}$$

The parameter γ was chosen to ensure that the dimensionless affine canonical transformations agree at the endpoints $x = 0, 1$ and the midpoint $x = 0.5$ which had the effect of greatly tightening the global fitness of the canonical curves.

In Ref. 16, it was also shown that the intrinsic connection between the canonical nature of molecular potentials and their associated force distributions has further fundamental implications. Specifically, the force distributions themselves were shown to have canonical decompositions. Moreover, the notion of canonical force distribution is of a more fundamental nature than canonical potential in that if force is canonical across a class of diatomic molecules, then so is potential, but the reverse implication is in general not true. That is, the fact that the potentials for a class of diatomic molecules have canonical decompositions does not, in general, imply that their associated force distributions do likewise.

In the present contribution, it is demonstrated that the above notion of canonical potential or force curve shape plays an even more fundamental role in the nature of the molecular bond than just the energy $E(R)$ and its associated force $F(R)$. To illustrated that role, it proves helpful to express the Virial Theorem written in the form:[10,11,17]

$$T(R) = W(R) - E(R) \tag{8}$$

$$V(R) = 2E(R) - W(R) \qquad (9)$$

$$W(R) = RF(R) \qquad (10)$$

$$E(R) = V(R) + T(R), \qquad (11)$$

in which $T(R)$, $V(R)$ and $W(R)$ denote the electronic kinetic energy, electrostatic potential energy and work (done by the Feynman Force). It can be shown that each of the energies $T(R)$, $V(R)$ and $W(R)$ also are canonical in the sense described above. Indeed, it was initially conjectured that the Feynman Force could be used to determine the sequence of nuclear separation distances that identify the canonical sections of the various energy curves. However, that conjecture proved to be incorrect; nature behaves somewhat differently. What emerged during the study of these energies, was that the canonical sections of each energy curve are identified by the generalized force associated with each energy. More specifically, the canonical sections of the electronic kinetic energy $T(R)$, the electrostatic potential energy $V(R)$ and work $W(R)$ curves are determined by their respective generalized force distributions

$$F_T(R) := -T'(R) \qquad (12)$$

$$F_V(R) := -V'(R) \qquad (13)$$

$$F_W(R) := -W'(R). \qquad (14)$$

In particular, the canonical sections of $E(R)$ and $F(R)$ do not correspond to the canonical sections of $T(R)$ or of $V(R)$ or of $W(R)$; the canonical sections of each of these energies are determined by each energy's own associated generalized force distribution.

A. Canonical Kinetic Energy

Demonstrating the canonical nature of the electronic kinetic energy $T(R)$ begins by selecting a reference molecule, which as was done in Ref. 13, 15, and 16, and is taken herein to be the simplest molecule H_2^+. The sequence of separation distances

$$\ldots < R_{r2}^{*T}(\alpha) < R_{r1}^{*T}(\alpha) < R_{r0}^{*T}(\alpha) < R_{e}^{*T} < R_{a0}^{*T}(\alpha) < R_{a1}^{*T}(\alpha) < R_{a1}^{*T}(\alpha) < \ldots \tag{15}$$

are then constructed according to Eqs. (2) and (3) but with the $F(R)$ in Eq. (1) replaced by the

generalized force Eq. (12) associated with the electronic kinetic energy $T(R)$. Figure 1 illustrates

how the generalized force $F_T(R)$ is used to identify the various canonical sections of the kinetic

energy curve.

1. Piecewise Affine Transformation to Canonical Dimensionless Form

The reference canonical forms for the kinetic energy $\tilde{T}_{aj}^{*}(x;\alpha)$ and $\tilde{T}_{rj}^{*}(x;\alpha)$, $j = 0, 1, \ldots$, with

for $0 \le x \le 1$, are defined by:

$$\tilde{T}_{a0}^{*}(x;\alpha) := \frac{T(xR_{a0}^{*T}(\alpha)+(1-x)R_{e}^{*T})-T(R_{e}^{*T})}{T(R_{a0}^{*T}(\alpha))-T(R_{e}^{*T})} \tag{16}$$

$$\tilde{T}_{aj}^{*}(x;\alpha) := \frac{T(xR_{aj}^{*T}(\alpha)+(1-x)R_{a(j-1)}^{*T}(\alpha))-T(R_{a(j-1)}^{*T}(\alpha))}{T(R_{aj}^{*T}(\alpha))-T(R_{a(j-1)}^{*T}(\alpha))}, \quad j > 0 \tag{17}$$

$$\tilde{T}_{r0}^{*}(x;\alpha) := \frac{T(xR_{r0}^{*T}(\alpha)+(1-x)R_{e}^{*T})-T(R_{e}^{*T})}{T(R_{r0}^{*T}(\alpha))-T(R_{e}^{*T})} \tag{18}$$

$$\tilde{T}_{rj}^{*}(x;\alpha) := \frac{T(xR_{rj}^{*T}(\alpha)+(1-x)R_{r(j-1)}^{*T}(\alpha))-T(R_{r(j-1)}^{*T}(\alpha))}{T(R_{rj}^{*T}(\alpha))-T(R_{r(j-1)}^{*T}(\alpha))}, \quad j > 0. \tag{19}$$

2. Inverse Canonical Transformation

The affine transformations Eqs. (16) – (19) are inverted by the formulas:

$$T^{*}(R) = T^{*}(R_{e}^{*T}) + \tilde{T}_{a0}^{*}(x;\alpha)\left(T(R_{a0}^{*T}(\alpha))-T(R_{e}^{*T})\right), \quad R_{e}^{*T} < R < R_{a0}^{*T}(\alpha) \tag{20}$$

$$T^{*}(R) = T^{*}(R_{a(j-1)}^{*T}(\alpha)) + \tilde{T}_{aj}^{*}(x;\alpha)\left(T(R_{aj}^{*T}(\alpha))-T(R_{a(j-1)}^{*T}(\alpha))\right), \quad R_{a(j-1)}^{*T}(\alpha) < R < R_{aj}^{*T}(\alpha) \tag{21}$$

$$T^{*}(R) = T^{*}(R_{e}^{*T}) + \tilde{T}_{r0}^{*}(x;\alpha)\left(T(R_{r0}^{*T}(\alpha))-T(R_{e}^{*T})\right), \quad R_{r0}^{*T}(\alpha) < R < R_{e}^{*T} \tag{22}$$

$$T^{*}(R) = T^{*}(R_{r(j-1)}^{*T}(\alpha)) + \tilde{T}_{rj}^{*}(x;\alpha)\left(T(R_{rj}^{*T}(\alpha))-T(R_{r(j-1)}^{*T}(\alpha))\right), \quad R_{rj}^{*T}(\alpha) < R < R_{r(j-1)}^{*T}(\alpha) \tag{23}$$

.

In Eqs. (20) – (23), x is defined, respectively, by:

$$
x = \begin{cases}
\dfrac{R - R_e^{*T}}{R_{a0}^{*T}(\alpha) - R_e^{*T}} & : \quad R_e^{*T} < R < R_{a0}^{*T}(\alpha) \\[3ex]
\dfrac{R - R_{a(j-1)}^{*T}(\alpha)}{R_{aj}^{*T}(\alpha) - R_{a(j-1)}^{*T}(\alpha)} & : \quad R_{a(j-1)}^{*T}(\alpha) < R < R_{aj}^{*T}(\alpha) \quad j > 0 \\[3ex]
\dfrac{R_e^{*T} - R}{R_e^{*T} - R_{r0}^{*T}(\alpha)} & : \quad R_{r0}^{*T}(\alpha) < R < R_e^{*T} \\[3ex]
\dfrac{R_{r(j-1)}^{*T}(\alpha) - R}{R_{r(j-1)}^{*T}(\alpha) - R_{rj}^{*T}(\alpha)} & : \quad R_{rj}^{*T}(\alpha) < R < R_{r(j-1)}^{*T}(\alpha) \quad j > 0.
\end{cases}
\tag{24}
$$

B. Canonical Electrostatic Potential Energy and Work

Demonstrating the canonical nature of the electrostatic potential energy $V(R)$ and the work $W(R)$ proceeds in precisely the same fashion as for the electronic kinetic energy $T(R)$. The key point is to use the generalized force distributions Eqs. (13) and (14) associated with $V(R)$ and $W(R)$ to define the critical separation distances in Eqs. (15) that enter into the various formulas. In the next section, these formulas are applied to the four molecules: H_2^+, H_2, HeH^+, and LiH with H_2^+ chosen as reference.

III. Results and Discussion

Figure 2 exhibits the four (dimensional) generalized energies $E(R)$, $T(R)$, $V(R)$, $W(R)$ and their associated force distributions for the four molecules H_2^+, H_2, HeH^+ and LiH. As a consequence of the Virial Theorem when $T(R)$ is zero, $E(R) = V(R) = W(R)$, and when $V(R)$ is zero, $E(R) = T(R)$. Similar relations hold for the associated generalized forces. It is pertinent to note that the generalized forces of $T(R)$ and $V(R)$ are both binding only inside the interval defined where each generalized force is zero. Before this interval, the generalized force for $T(R)$ is anti-

binding and the generalized force for $V(R)$ is binding. After this interval the generalized force for $T(R)$ is binding and the generalized force for $V(R)$ is anti-binding.

Tables 1 – 4 list the inter-nuclear separation distances associated to each of the four generalized energies $E(R)$, $T(R)$, $V(R)$, and $W(R)$. Figure 3 exhibits the canonical nature of the (dimensionless) electronic kinetic energy curves given by Eqs. (16) – (19) and (24) corresponding to sections of the dimensional electronic kinetic energy curves in Figure 2. The relative errors in these figures, and the corresponding for $V(R)$ and $W(R)$, are listed in Tables 5 – 7 where the relative error is defined to be the ratio of the absolute error to the accurate value. The relative errors on all piecewise canonical segments for $T(R)$, $V(R)$, and $W(R)$ are less than the very small value of 0.0095 and include a correction for the γ parameter. The corresponding data in the figures is illustrative and do not include a correction for the γ parameter.

It should be noted that the canonical nature of the electronic kinetic energy is not at all evident from the dimensional curves appearing in Figure 2; indeed, it gets revealed through the piecewise affine transformations to canonical form given by Eqs. (16) – (19) and (24) as shown in Figure 3. Of equal importance is the use of the inverse transformations Eqs. (20) – (23) (as exploited in Ref. 13 for $E(R)$) to construct formulations of the electronic kinetic energy curves for the molecules H_2, HeH^+ and LiH as piecewise affine transformations of the electronic kinetic energy curve for the reference molecule H_2^+. Moreover, the generalized energies $E(R)$, $T(R)$, $V(R)$, and $W(R)$ for any diatomic molecule can be generated from the generalized energies of the reference molecule, H_2^+. The latter, however, is dependent on sufficient independent data being available from another independent source whether generated by experiment or alternative computational methods.

Figure 4 exhibits the somewhat unexpected result that the canonical sections of the electronic kinetic energy $T(R)$, electrostatic potential energy $V(R)$, and work $W(R)$ for H_2^+ are nearly identical. Importantly, the various canonical sections for $T(R)$, $V(R)$, and $W(R)$ are determined by their associated generalized forces $F_T(R)$, $F_V(R)$, and $F_W(R)$, and hence correspond to different $R-$intervals. Relative errors in these curves are given in Tables 8 and 9 and include a correction for the γ parameter as described previously. The agreement of these canonical energies with that for the canonical total energy $E(R)$ is also surprisingly good except for the first sections on either side of the equilibrium separation. It is significant to emphasize that the Virial Theorem [Eqs. (8) $-$ (11)] does not hold for the canonical forms of the various energies but hold only for the dimensional forms of the energies. It is also important to remark that close agreement among the various dimensionless canonical forms for these four energies implies that any one of them can be used to construct dimensional approximations of the others through piecewise affine scaling with very small relative error. (*cf*. Ref. 13). Thus, for example, $T(R)$ can be used to construct accurate dimensional approximations to $V(R)$ and $W(R)$ as illustrated in Figure 5. In Figure 5, the inverse canonical transformation is used to approximate $V(R)$ and $W(R)$ for H_2^+ on the bottom of the well between the two separation distances (less than and greater than the equilibrium separation at which the generalized force is zero) where the generalized force equals its maximum value using piecewise affine scaling of $T(R)$. For $V(R)$, the relative error is only 0.00048 and for $W(R)$, the relative error is only 0.00061.

The canonical nature of the four energies $E(R)$, $T(R)$, $V(R)$, and $W(R)$ suggest an intriguing perspective for formulating a classification scheme for bonding characteristics in diatomic molecules. In particular, while each of these energies have corresponding dimensionless forms that are canonical across a broad range of diatomic molecules, the inter-relationships among their

dimensional forms for a given molecule are not canonical. More specifically, the inter-relationships among the sequences of separation distances used to identify canonical dimensionless sections of each energy and the specific dimensional forms for their associated generalized forces manifest important non-canonical characteristics of bond formation for a given molecule. A detailed investigation and application of these ideas will be the subject of a future study.

IV. Conclusions

Application of canonical approaches has given a fundamentally new perspective on bonding in H_2^+, H_2, HeH^+ and LiH and thus potentially in other molecular systems. The semi-empirical demonstration of the canonical nature of $E(R)$, $F(R)$, $T(R)$, $V(R)$, $W(R)$ and their derivatives to high accuracy in these systems gives confidence for further applications of this approach. The demonstration of the canonical nature of $T(R)$, $V(R)$, and $W(R)$ have particular significance in the understanding of molecular bonding in these systems. The canonical perspective of $F(R)$ has been confirmed semi-empirically recently[16] and when combine with the Virial Theorem give additional fundamentally new quantitative insights into the nature of bonding in the systems investigated. It has been demonstrated that the fundamentals functions in the Virial Theorem, which give considerable information about bonding, are independently canonical for the systems investigated.

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Table 1. Inter-nuclear separations for $E(R)$.

Molecule	$R_{er}(2)$	R_{efmr}	R_{em}	R_{efma}	$R_{ea}(1)$	$R_{ea}(2)$
H_2	0.5898	0.64751	0.7414	1.1342	1.7877	2.1205
HeH^+	0.6627	0.7064	0.7743	1.0331	1.4771	1.7431
LiH	1.3213	1.4270	1.5949	2.2820	3.4180	3.8935
H_2^+	0.8507	0.9292	1.0569	1.5967	2.6161	3.2039

Table 2. Inter-nuclear separations for $T(R)$.

Molecule	$R_{tr}(2)$	R_{tfmr}	R_{tm}	R_{tfma}	$R_{ta}(1)$	$R_{ta}(2)$
H_2	1.2068	1.3517	1.5408	2.0200	2.5919	2.9084
HeH^+	1.0613	1.1318	1.2339	1.5606	2.0410	2.3312
LiH	2.1738	2.4874	2.9368	3.7260	4.4183	4.8408
H_2^+	1.8337	2.0235	2.2922	3.0943	4.1713	4.7755

Table 3. Inter-nuclear separations for $V(R)$.

Molecule	$R_{vr}(2)$	R_{vfmr}	R_{vm}	R_{vfma}	$R_{va}(1)$	$R_{va}(2)$
H_2	1.4837	1.5986	1.7478	2.1587	2.7081	3.0233
HeH^+	1.2221	1.2888	1.3841	1.6902	2.1573	2.4458
LiH	2.5864	2.8837	3.20731	3.8164	4.5045	4.9275
H_2^+	2.3248	2.4906	2.7221	3.4369	4.4699	5.0682

Table 4. Inter-nuclear separations for $W(R)$.

Molecule	$R_{wr}(2)$	R_{wfmr}	R_{wm}	R_{wfma}	$R_{wa}(1)$	$R_{wa}(2)$
H_2	0.9759	1.1121	1.3191	1.8823	2.48677	2.8061
HeH^+	0.9479	1.4537	1.1164	1.4537	1.9449	2.2356
LiH	1.9163	2.1554	2.5851	3.6317	4.3559	4.7719
H_2^+	1.4509	1.6203	1.8859	2.7639	3.8999	4.5125

Table 5. Relative errors for electronic kinetic energy, $T(R)$.

Molecule	$R_{tr}(2) - R_{tr}(1)$	$R_{tr}(1) - R_{tm}$	$R_{tm} - R_{tfm}$	$R_{tfm} - R_{ta}(1)$	$R_{ta}(1) - R_{ta}(2)$
H_2	0.0061	0.0092	0.0025	0.00038	0.000019
HeH^+	0.0042	0.0044	0.00094	0.00092	0.00044
LiH	0.0050	0.0016	0.0062	0.0021	0.0014

Table 6. Relative errors for electrostatic potential energy, $V(R)$.

Molecule	$R_{vr}(2) - R_{vr}(1)$	$R_{vr}(1) - R_{vm}$	$R_{vm} - R_{vfm}$	$R_{vfm} - R_{va}(1)$	$R_{va}(1) - R_{va}(2)$
H_2	0.0085	0.0062	0.0016	0.00025	0.000018
HeH^+	0.0023	0.0037	0.00055	0.00072	0.00043
LiH	0.0047	0.0035	0.0062	0.00204	0.0026

Table 7. Relative errors for virtual work, $W(R)$.

Molecule	$R_{wr}(2) - R_{wr}(1)$	$R_{wr}(1) - R_{wm}$	$R_{wm} - R_{wfm}$	$R_{wfm} - R_{wa}(1)$	$R_{wa}(1) - R_{wa}(2)$
H_2	0.0078	0.0047	0.0026	0.00059	0.000014
HeH^+	0.0063	0.0028	0.00018	0.00013	0.00045
LiH	0.0039	0.0022	0.0027	0.00090	0.0025

Table 8. Relative errors between $E(R)$ and the other energies $T(R)$, $V(R)$ and $W(R)$ for H_2^+.

	$R_r(2) - R_r(1)$	$R_r(1) - R_m$	$R_m - R_a(1)$	$R_a(1) - R_a(2)$
$T(R)$	0.00094	0.015	0.035	0.0013
$V(R)$	0.0011	0.015	0.03	0.00077
$W(R)$	0.00014	0.0063	0.03	0.002

Table 9. Relative errors between $T(R)$, $V(R)$ and $W(R)$ for H_2^+.

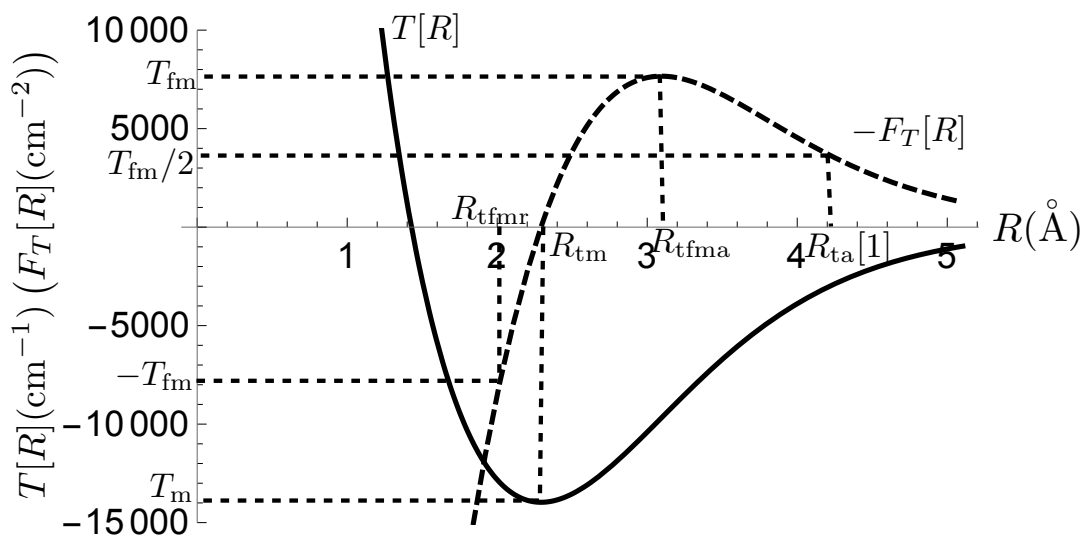|	$R_r(2) - R_r(1)$	$R_r(1) - R_m$	$R_m - R_a(1)$	$R_a(1) - R_a(2)$
$V(R)$	0.0002	0.0001	0.0052	0.00061
$W(R)$	0.0008	0.0089	0.0054	0.00076

Figure 1. Electronic kinetic energy and its generalized force distribution, for the H_2^+ molecule.
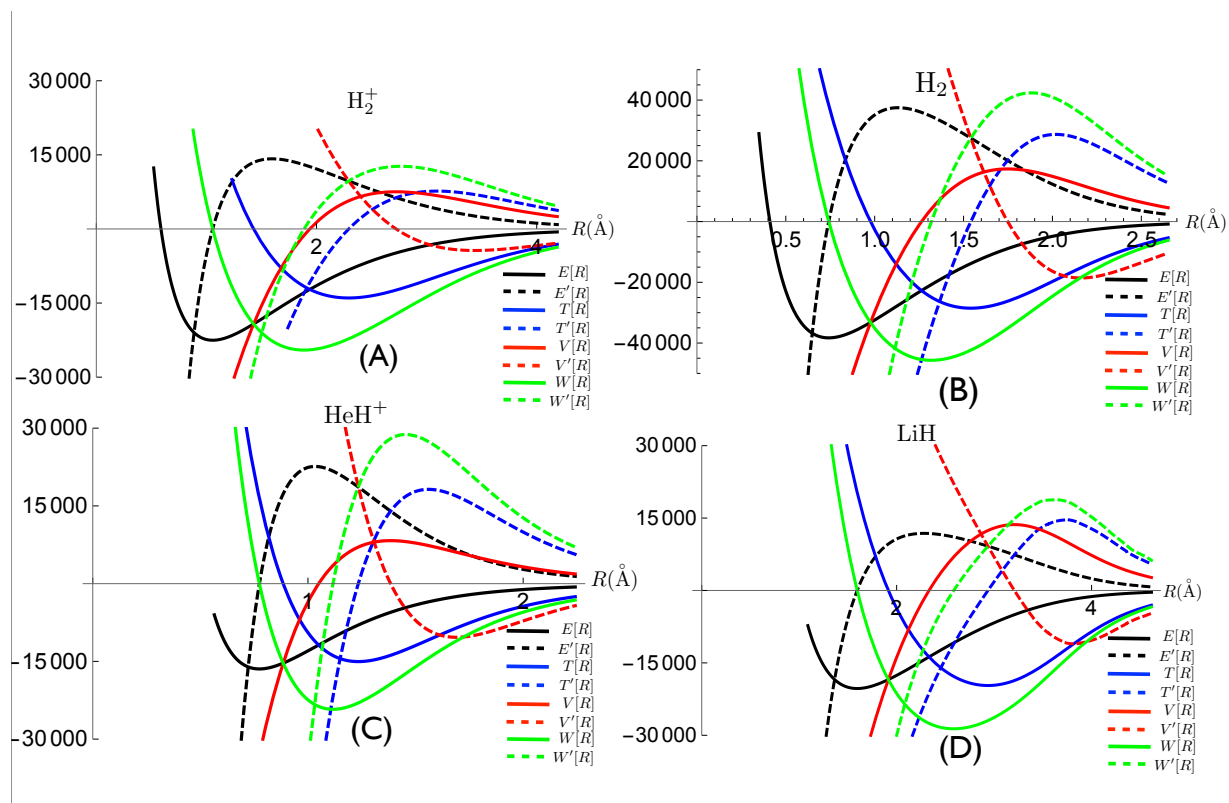
Figure 2. The Viral Theorem functions ($E(R)$, $T(R)$, $V(R)$, and $W(R)$)) and their respective generalized force distributions for: (A) H_2^+, (B) H_2, (C) HeH^+, (D) LiH.
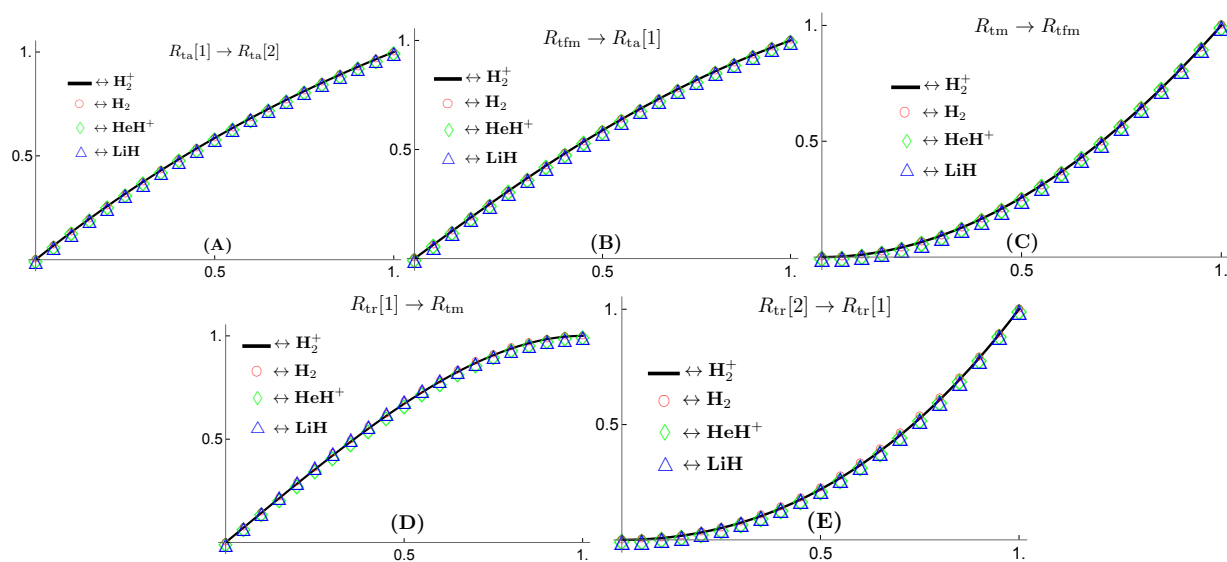
Canonical Kinetic Energy

Figure 3. Canonical electronic kinetic energy for H_2^+ (solid black curve), H_2 (red circles), HeH^+ (green diamond), and LiH (blue triangle). Panels (A) to (E) correspond to different piecewise segments.
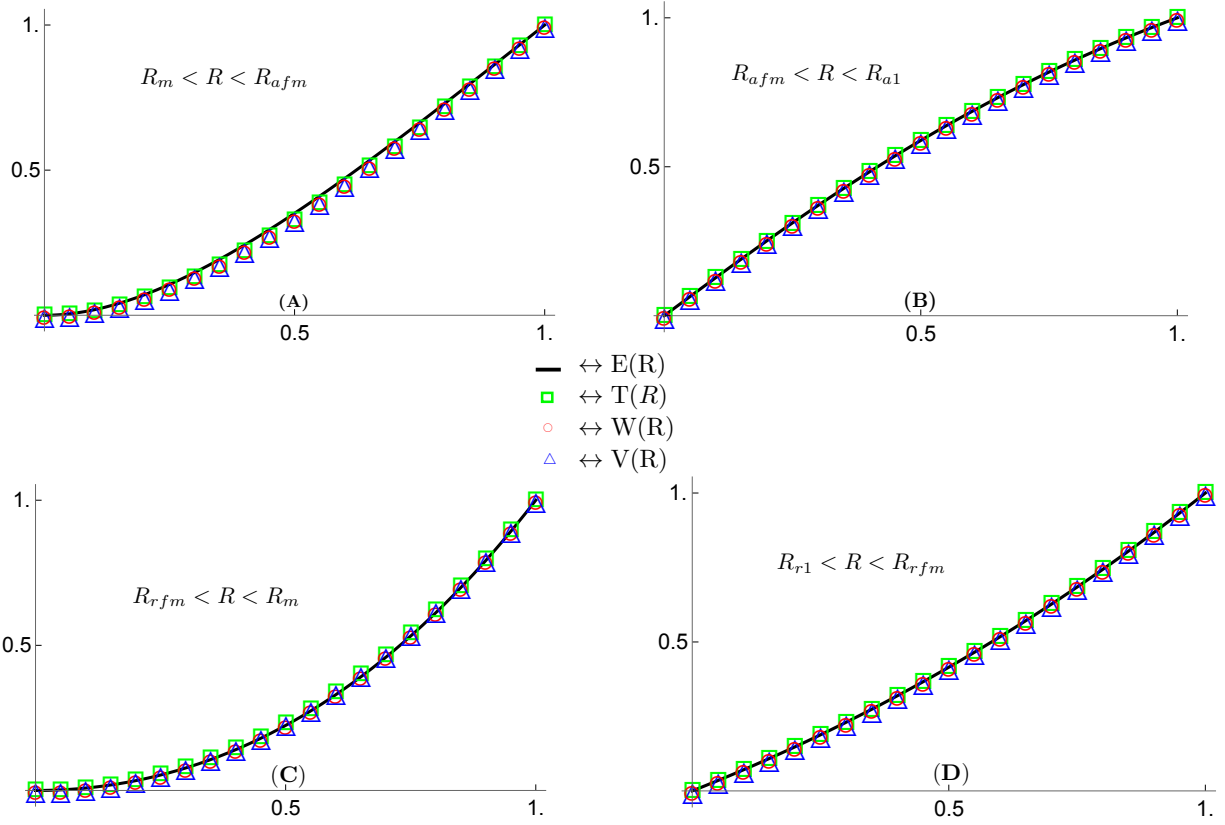
Figure 4. Comparison of four dimensionless sections of the four canonical energies for H_2^+. (A) The canonical section from R_m (the separation distance at which the generalized force is zero) to R_{afm} (the separation distance at which a given generalized attractive force attains its maximum value); (B) The canonical section from R_{afm} to R_{a1} (the separation distance at which a given generalized attractive force is diminished to half of its maximum value); (C) and (D) are the corresponding sections on the repulsive side of the equilibrium separation distance.
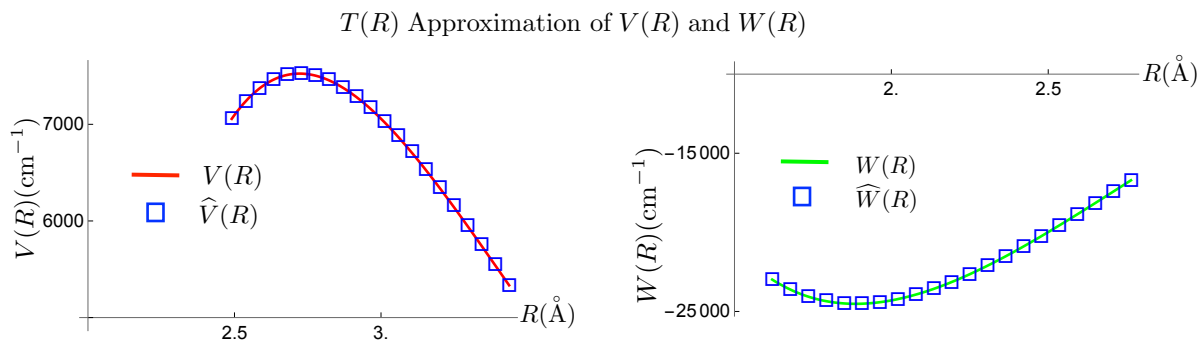
Figure 5. Left panel show the approximate curve for $V(R)$ (blue squares) for H_2^+ compared to the accurate value (red curve). Right panel show the approximate curve for $W(R)$ (blue squares) for H_2^+ compared to the accurate value (green curve). For both panels, the approximate curves were generated by the inverse canonical transformation and piecewise affine scaling of $T(R)$.

Table of Contents Graphic

Canonical Electronic Kinetic Energy

$\leftrightarrow$ H_2^+

$\bigcirc$ $\leftrightarrow$ H_2

$\diamond$ $\leftrightarrow$ HeH^+

$\triangle$ $\leftrightarrow$ LiH