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Canonical Force Distributions in Pairwise Interatomic Interactions from the Perspective of the Hellmann-Feynman Theorem

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Abstract

In recent work, force-based canonical approaches have given a unified but different viewpoint on the nature of bonding in pairwise interatomic interactions. The concept of a pairwise canonical potential in these cases was defined for a class of molecules referred to a dimensionless function obtained from each molecule by a readily invertible algebraic transformation. Differing molecular categories (covalent, ionic, van der Waals, hydrogen and halogen bonding) of representative interatomic interactions in which binding energies ranging from 1.01 to 1072.03 kJ/mol have been modeled canonically giving a rigorous semi-empirical verification to high accuracy. However, the fundamental physical basis that is expected to provide the inherent characteristics of these canonical transformations have not yet been elucidated. We now show that canonical force distributions can be formulated from the perspective of the Hellmann-Feynman Theorem and discuss how such canonical approaches can be used to further explain the nature of chemical bonding in pairwise interatomic interactions.

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I. Introduction

It has been conjectured that the query, *How do molecules form?*, should still be regarded as one of the most profound scientific questions remaining in Chemistry [1]. Models of the nature of chemical bonding are still the subject of considerable investigation even after the fundamental principles of quantum mechanics were first established in the period 1924-1927. Much of these initial developments attributed to Heitler and London [2], Pauling [3], Mulliken and Hund [4] have now lead to increasingly wider range of quantum chemistry approaches to molecular structure, molecular dynamics, and chemical reactions [5-8]. Although, the molecular-orbital approach has now become the most widely accepted, there is still no a general agreement among chemists [9] that this is the best approach to chemical bonding. Ball has stated [1], *that this model of molecules and all others are based on simplifying assumptions and are thus approximate, partial descriptions*. As a result, the choice of quantal description of the chemical bond remains the subject of active discussion [9]. Though modern molecular computational methods can capture most situations associated with effects such as correlation energy, none can give an exact solution [10].

Approaches to quantum mechanics that have the potential to improve the situation described in the previous paragraph, are thus of particular interest. In this context, is the method initially advocated by Slater to pairwise interatomic interactions study molecular bonding through application of the Virial Theorem [11,12] and its subsequent relationship to the Hellmann-Feynman Theorem [13,14] strictly within the Born-Oppenheimer approximation [15,16].

Recently, we introduced the concept of a pairwise canonical potential [17] defined for a class of molecules referred to a dimensionless function obtained from each molecule by a readily invertible algebraic transformation. Differing categories (covalent, ionic etc.) of representative

interatomic interactions with binding energies ranging from 1.01 to 1072.03 kJ/mol were accurately modeled canonically to give a more unifying perspective that included diatomics CO, N₂, H₂⁺, H₂, HF, LiH, Mg₂, Ca₂, O₂, Ar₂, and in one-dimensional (1-D) dissociative coordinates morphed potentials of OC-HX [X = F, Cl, Br, I], OC-HCCH, OC-HCN, OC-BrCl, and OC-Cl₂, selected to illustrate intermolecular hydrogen and halogen bonding. A 1-D potential energy approach based on the renowned Rydberg-Klein-Rees method was later found to surprisingly require no adjustable parameters [17]. *Explicit* generalizations to all pairwise interactions studied, even at the asymptotic limit and extremely accurate strictly Born-Oppenheimer calculations have now been referenced to H₂⁺ [18,19]. Mapping to a canonical 1-D potential resulted in a unifying approach encompassing a prior statement of Slater [20] while giving a rigorous semi-empirical verification. Functions associated with the diatomic Virial Theorem ($E(R)$, $F(R)$, $V(R)$, $T(R)$, $W(R) = RF(R)$) were also shown recently to be individually canonical giving further perspectives into the nature of chemical bonding [21].

However, the question arises, is there a basis for this defined canonical approach in fundamental quantum molecular physics? In this work, we shall now demonstrate that applications of canonical transformations to diatomic molecules within the Born-Oppenheimer approximation can indeed be understood from this perspective. This force-based canonical approach will be demonstrated in the context of the Hellmann-Feynman Theorem (1937, 1939) [13,14], one of the most fundamental equations of molecular quantum mechanics that is quantum mechanically exact. The latter will be shown to be a significant issue for explaining development of the canonical methodology and establishing directions for its future applications. Our formulations will further be shown to have distinct advantages for modeling molecular bonding in general. We shall, in addition, discuss these developments in the light of Dirac's quotation

regarding *mathematics of transformations in quantum mechanics* [cf. Preface, Principles of Quantum Mechanics, 1930] [22].

II. Methods

A. Relevant Aspects of the Hellmann-Feynman Theorem

The objective behind this contribution is to identify physical principles underlying recently developed canonical forms and transformations relating potentials and their associated generalized forces in diatomic molecules and certain molecular complexes within the 1-D dissociative coordinate [18,19,21,23,24,25]. These various canonical forms and transformations can all be considered as bearing a fundamental relationship to the well-known *Feynman force*. The Feynman force is the virtual (steady-state) force acting on a nucleus within a molecule under the idealized Born-Oppenheimer approximation that all nuclei occupy fixed positions. As discussed by Feynman (1939) [14], the virtual force of interest acting upon a fixed nucleus is minus the derivative of the ground-state energy with respect to a (scalar) parameter λ associated with the position of the nucleus. The seminal result in this landmark paper is the celebrated Hellmann-Feynman Theorem [13,14]:

$$f_{\lambda} = -\left\langle \psi \left| \frac{\partial H}{\partial \lambda} \right| \psi \right\rangle = -\int \psi^* \frac{\partial H}{\partial \lambda} \psi \, dv \quad (1)$$

where $f_{\lambda} = -\frac{\partial U}{\partial \lambda}$ with H and ψ denoting the Hamiltonian and wave function, respectively, and

U is the eigenvalue (energy) defined by $H\psi = U\psi$ from which it follows that: $U = \langle \psi | H | \psi \rangle$.

Feynman observes further that $\partial H / \partial \lambda = \partial V / \partial \lambda$ where V is the potential energy portion of the Hamiltonian that involves only classical Coulombic interactions among the chosen fixed nucleus,

the other (fixed) nuclei and each of the electrons. In particular, $\partial H / \partial \lambda = \partial V / \partial \lambda$ does not involve electron-electron interactions. Feynman then goes on to show how the integral in Eq. (1) can be replaced by integration against the net charge density distribution over 3-space rather than integration over $3N$ -space, where N is the number of electrons, as straight-forward application of Eq. (1) seems to require.

B. Details of Charge Density Calculations

The charge density calculations were performed using MOLPRO, version 2012.1 [26,27]. For H_2^+ the charge density was calculate using spin-unrestricted Hartree-Fock (UHF) and the cc-pV8Z basis set [28] without the k orbital. For H_2 the charge density was calculate using full configuration interaction (FCI) [29,30] and the cc-pV6Z basis set. Table 1 lists the interatomic separations at which the H_2^+ and H_2 charge densities were calculated. For both molecules and for each interatomic separation, the charge density was calculate on a 2-D grid of 8,001 points on the x - z plane ($y = 0$) from -8.0 to 8.0 Bohr on x and z directions and step size of 0.002 Bohr. This fine 2-D grid for the charge density is necessary to numerically accurately solve the integral in Eq. (2) below.

C. Evaluation of the Feynman Force for H_2 and H_2^+

For reasons previously discussed, particularly those associated with accuracy, we shall first consider applications to the two simplest diatomic molecules H_2 and H_2^+ . More specifically, we will use the Hellmann-Feynman theorem to calculate the Feynman force acting at one of the two nuclei for each of these molecules. In our previous works [18,19,23,24] on canonical forms and transformations for these molecules, we showed the pivotal role the Feynman force plays in their construction, and to that end, the Feynman force was calculated by differentiation of accurate ground-state potentials taken from the literature. For the parameter λ , we take the interatomic

separation distance R and we adopt a Cartesian coordinate system centered equidistant between the two nuclei located at $(0,0,\pm R/2)$ in the (x,y,z) Cartesian frame. Relative to this Cartesian frame, the Feynman force for H_2 acting upon the right nucleus takes the form (in atomic units):

$$F(R) = \frac{1.0}{R^2} - \int_{\mathbb{R}^3} \rho(x,y,z;R) \frac{(z - R/2)}{(x^2 + y^2 + (z - R/2)^2)^{3/2}} dv \quad (2)$$

where $\rho(x,y,z;R)$ denotes the net charge density distribution (corresponding to both electrons) for the interatomic separation distance R . The first term in Eq. (2) is the (repulsive) force on the nucleus at the point $(0,0,R/2)$ due to the nucleus at $(0,0,-R/2)$ where as the integral term is the (attractive) force on the (right) nucleus due to a single electron.

Relevant Remarks:

- i. A key observation is that Eq. (2) can be generalized to any pairwise interatomic interaction in their bound ground electronic state [31]. As an example in this work, we are applying Eq. (2) to the simplest molecules, H_2 and H_2^+ , because their very accurate charge density distributions can be calculated.
- ii. Eq. (2) is also the Feynman force for H_2^+ with the charge density distribution $\rho(x,y,z;R)$ for the two electron system H_2 replaced by the charge density distribution for the single electron system H_2^+ .
- iii. It is also helpful to appeal to the axial symmetry in H_2 and H_2^+ to reduce the 3-D integration in Eq. (2) to a 2-D integration in cylindrical coordinates.

D. Applications of Canonical Forms and Transformations for Potentials

In a sequence of recent papers [18,19,23,24], a notion of piecewise affine transformation to dimensionless canonical form was developed and applied to potentials corresponding to a wide class of diatomic molecules and pairwise intermolecular complexes. The basic affine

transformation of a dimensional section of a potential curve $E(R)$ for $R_1 \leq R \leq R_2$ to a canonical dimensionless curve has the form:

$$\tilde{E}(x; R_1, R_2) := \frac{E(R_1 + x(R_2 - R_1)) - E(R_1)}{E(R_2) - E(R_1)} \quad \text{for } 0 \leq x \leq 1. \quad (3)$$

The inverse transformation corresponding to Eq. (3) allows the original dimensional potential $E(R)$ to be written in terms of its dimensionless canonical counterpart $\tilde{E}(x)$ by the formula:

$$E(R) = E(R_1) + (E(R_2) - E(R_1)) \tilde{E}\left(\frac{R - R_1}{R_2 - R_1}\right). \quad (4)$$

Two potential functions $E_1(R)$ and $E_2(R)$ are said to be canonical if there exist sequences of points $\{R_{1,1} < R_{1,2} < \dots < R_{1,N}\}$ and $\{R_{2,1} < R_{2,2} < \dots < R_{2,N}\}$ for $E_1(R)$ and $E_2(R)$, respectively, so that the canonical forms $\tilde{E}_1(x; R_{1,j}, R_{1,j+1})$ and $\tilde{E}_2(x; R_{2,j}, R_{2,j+1})$ agree to a specified accuracy for $j = 1, 2, \dots, N-1$. The key for selecting these sequences of points was shown in [18,19,23,24] to rest fundamentally upon the associated Feynman forces: $F_1(R) := -E_1'(R)$ and $F_2(R) := -E_2'(R)$. Applying Eq. (4) to $E_1(R)$ for $R_{1,j} < R < R_{1,j+1}$ together with the approximation $\tilde{E}_1(x) \approx \tilde{E}_2(x)$ for $0 \leq x \leq 1$, one obtains:

$$\begin{aligned} E_1(R) &= E_1(R_{1,j}) + (E_1(R_{1,j+1}) - E_1(R_{1,j})) \tilde{E}_1\left(\frac{R - R_{1,j}}{R_{1,j+1} - R_{1,j}}\right) \\ &\approx E_1(R_{1,j}) + (E_1(R_{1,j+1}) - E_1(R_{1,j})) \tilde{E}_2\left(\frac{R - R_{1,j}}{R_{1,j+1} - R_{1,j}}\right). \end{aligned} \quad (5)$$

Relevant Remarks:

iv. Formula in Eq. (5) gives an affine scaling of the section

$S_{2,j} := \{(R, E_2(R)) | R_{2,j} \leq R \leq R_{2,j+1}\}$ for the potential curve $E_2(R)$ onto the

corresponding section $S_{1,j} := \{(R, E_1(R)) | R_{1,j} \leq R \leq R_{1,j+1}\}$ for the potential curve $E_1(R)$. This affine scaling maps the endpoints of the section $S_{2,j}$ to the endpoints of the section $S_{1,j}$ and otherwise maps the interval $R_{2,j} \leq R \leq R_{2,j+1}$ linearly onto the interval $R_{1,j} \leq R \leq R_{1,j+1}$. In this way, if the error in the approximation in Eq. (5) is below a specified tolerance, the two sections $S_{1,j}$ and $S_{2,j}$ are declared to have the same *shape*.

- v. Performing the construction in Eq. (5) for each $j=1, \dots, N-1$ gives a piecewise affine transformation of the potential curve $E_2(R)$ for $R_{2,1} \leq R \leq R_{2,N}$ onto the potential curve $E_1(R)$ for $R_{1,1} \leq R \leq R_{1,N}$. The two potential curves $E_1(R)$ and $E_2(R)$ are then declared to have the same *canonical shape*.

E. Applications of Canonical Forms and Transformations for Force

In [25], it was demonstrated that the Feynman forces associated with two canonical potentials are also canonical. Indeed, it was argued in [25] that the notion of canonical Feynman force was more fundamental than the previously described canonical potential. In [25], the Feynman force for a given molecule was calculated by direct differentiation of a piecewise spline curve interpolated to discrete points on the associated potential curve obtained from highly accurate first principle numerical calculation. However, as is well known, numerical differentiation of this sort can give very large errors in the computed derivative even if the potential data points used give a highly accurate approximation to the accurate potential curve. In this contribution, we demonstrate that appealing to the Hellmann-Feynman theorem avoids this difficulty, and perhaps even more importantly, it gives valuable insight into the nature of the canonical shapes of

potential curves and their associated Feynman force distributions that have been shown in [18,19,23,24,25].

III. Results

Figure 1 shows the Feynman force curves for H_2 (solid black curve) and H_2^+ (dashed blue curve) (in SI units) derived from Eq. (2) (in atomic units) computed by application of the Hellmann-Feynman theorem. Each Feynman force curve is divided into three sections denoted I, II, III that have the same *canonical shape* in the sense defined previously. The solid red and blue dots on the abscissa give the R -values, labeled in ascending order $\{R_1 < R_2 < R_3 < R_4\}$, corresponding to the endpoints of the three curve sections for H_2 and H_2^+ , respectively. The algorithm for determining these endpoints for each Feynman force curve is as follows.

First R_2 is chosen to be the bottom of the well for each Feynman force curve, that is, the nuclear separation distance corresponding to the maximum (in magnitude) of the attractive Feynman force, denoted F_m . For H_2 , R_1 is chosen to be the nuclear separation at which the repulsive force equals F_m , that is, $F(R_1) = F_m$. Then R_3 and R_4 are the nuclear separation distances at which the attractive Feynman force has magnitude one-half and one-quarter of the maximum value, that is, $|F(R_3)| = F_m/2.0$ and $|F(R_4)| = F_m/4.0$. In Figure 1, these points are labeled with solid red dots as: $R_1 = R_{rm}$, $R_2 = R_{am}$, $R_3 = R_{a1}$, and $R_4 = R_{a2}$. To determine the corresponding points for H_2^+ , it is convenient now to declare $F_1(R)$ and $F_2(R)$ to be the Feynman force curves for H_2 and H_2^+ , respectively.

For each section I, II and III, one defines the associated dimensionless canonical form for H_2 :

$$\tilde{F}_{1,j}(x) = \frac{F_1(R_{1,j} + x(R_{1,j+1} - R_{1,j})) - F_1(R_{1,j})}{F_1(R_{1,j+1}) - F_1(R_{1,j})} \quad \text{for } 0 \leq x \leq 1. \quad (6)$$

For H_2^+ , Eq. (6) takes the somewhat more general form:

$$\tilde{F}_{2,j}(x;\gamma_j) = \frac{F_2(R_{2,j}(\gamma_j) + x(R_{2,j+1}(\gamma_{j+1}) - R_{2,j}(\gamma_j))) - F_2(R_{2,j}(\gamma_j))}{F_2(R_{2,j+1}(\gamma_{j+1})) - F_2(R_{2,j}(\gamma_j))} \quad \text{for } 0 \leq x \leq 1 \quad (7)$$

in which the $R_{2,j}(\gamma_j)$ are defined by as follows. $\gamma_2 = 1$ and $R_{2,2}(\gamma_2) = R_{am}$, that is, the nuclear separation distance for H_2^+ for which the (attractive) Feynman force has its maximum magnitude (well bottom). The other $R_{2,j}(\gamma_j)$ values are defined by:

$$R_{2,1}(\gamma_1) = \gamma_1 R_{rm} + (1 - \gamma_1) R_{am} \quad (8)$$

$$R_{2,3}(\gamma_3) = \gamma_3 R_{a1} + (1 - \gamma_3) R_{am} \quad (9)$$

$$R_{2,4}(\gamma_4) = \gamma_4 R_{a2} + (1 - \gamma_4) R_{2,3}(\gamma_3). \quad (10)$$

The γ_j values for $j = 1, 3, 4$ are chosen to satisfy:

$$\tilde{F}_{2,j}(0.5;\gamma_j) = \tilde{F}_{1,j}(0.5). \quad (11)$$

Hence, the two dimensionless canonical forms $\tilde{F}_{1,j}(x)$ and $\tilde{F}_{2,j}(x;\gamma_j)$ agree at the three points $x = 0, 0.5, 1.0$. This effects a small shift in the R_j values for F_2 and serves merely to decrease the agreement error a small amount between $\tilde{F}_{1,j}(x)$ and $\tilde{F}_{2,j}(x)$. Table 2 gives the resulting R_j values. The number in parentheses for H_2^+ correspond to setting $\gamma_j = 1.0$.

The blue circles on the solid black curve in Figure 1 correspond to the piecewise affine approximation of the Feynman force for H_2 constructed constructed from the Feynman force curve for H_2^+ according to the formula:

$$\begin{aligned}
F_1(R) &= F_1(R_{1,j}) + \left(F_1(R_{1,j+1}) - F_1(R_{1,j}) \right) \tilde{F}_1 \left(\frac{R - R_{1,j}}{R_{1,j+1} - R_{1,j}} \right) \\
&\approx F_1(R_{1,j}) + \left(F_1(R_{1,j+1}) - F_1(R_{1,j}) \right) \tilde{F}_2 \left(\frac{R - R_{1,j}}{R_{1,j+1} - R_{1,j}}; \gamma_j \right)
\end{aligned} \tag{12}$$

for $R_{1,1} \leq R \leq R_{1,4}$ and with $j = 1, 2,$ and 3 . Table 3 gives the relative errors between $F_1(R)$ and the approximation given in Eq. (12) where the relative error between two functions $f_1(r)$ and $f_2(r)$ over an interval $a \leq r \leq b$ is defined by:

$$\text{Rel. Err.} = \frac{\int_a^b |f_1(r) - f_2(r)| dr}{\int_a^b |f_1(r)| dr}. \tag{13}$$

It is worth noting that section I for the Feynman force curves for both H_2 and H_2^+ is half on the repulsive side of equilibrium and half on the attractive side, yet the affine scaling of the Feynman force curve for H_2^+ (with two electrons) onto the Feynman force curve for H_2 (with a single electron) agrees within a very small relative error of 0.000857 which corresponds approximately to an average standard deviation of 4 parts in 10,000. Hence, their Feynman force curves have essentially the same canonical shape.

IV. Discussion

The block diagram in Figure 2 articulates the contributions that the different approaches make to understanding of force-based canonical transformations. It illustrates that the choice of H_2^+ as the reference molecular system is the most expedient. Although there is inadequate experimental information available to determine its accurate Born-Oppenheimer potential semi-empirically, it is a one-electron system where there is the possibility of determining ultra accurate ground state wave functions in the Hartre-Fock limit. In this case, using the cc-pV8Z

basis set (without the k orbital) we can also determine the corresponding Born-Oppenheimer potential function although in these particular calculations it is not needed. The determined wave function of H_2^+ is then available to accurately calculate its charge density distribution in the ground state potential. This charge density distribution is then used to calculate the accurate Feynman force (Section II.C) that can be also be directly calculated using the method of taking the negative of the derivative of the potential (Section II.E). The latter could be determined from accurate Born-Oppenheimer potentials either from exceptionally accurate theory or from extensive experimental data for the pairwise interatomic interactions.

The relative errors between the accurate sections I, II, III of the Feynman force curve for H_2 in Figure 1 and the approximations constructed using the corresponding sections from the Feynman force curve for H_2^+ in Figure 1 are given in Table 3. It is noteworthy that the relative errors correspond to twice the average standard deviation and that they are to parts in 10,000, an exceptional accuracy. This result also confirms that the fundamental role which the Feynman force plays in molecular quantum mechanics and its canonical characteristics. Furthermore, this work confirms the exceptional accuracy using the currently used Hellmann-Feynman approach for determination of force distributions and the corresponding canonical transformations.

Taken in its more general sense, Dirac has previously proposed that *quantum mechanics is primarily a theory of transformations* [22]. The proposed canonical approaches and corresponding transformations very much reflect the sentiment of this statement. The intense effort to find algebraic forms for reduced [32] and universal functions [33-35] can in certain respects be regarded as transformation approaches but of a distinctly different kind to that of the canonical approach described as the former invariably involve adjustable parameters that can not be directly related to physical measurable quantities. The application of transformations relating

potentials that are exact solutions to the Schrödinger equation is a well developed approach in supersymmetric quantum mechanics following the discovery of Gedenstein's theorem [5]. In this respect, the development of PCT approaches [36,37] is interesting but distinctly different as they are related only to potentials that are exact solutions of the Schrödinger equation. Figure 2, gives an overview of the current approach and in particular, its direct relation to the Hellmann-Feynman theorem. The development of the current canonical approaches are fundamentally based in molecular quantum mechanics and are, moreover, measurement based. Also, once the transformation for the simplest molecule H_2^+ is determined accurately, it is then available to generate the remainder of pairwise interatomic interactions with great accuracy provided that they are considered within the Born-Oppenheimer approximation as shown in Figure 2. However, what is startling in the current approach is that it is force-based at its most fundamental level. Once the transformations for H_2^+ are determined there is no need for additional adjustable parameters.

The schematic in Figure 2 also gives the rationale for explaining the previous canonical transformation approaches that were verified semi-empirically to high accuracy for a wide range of pairwise interatomic interactions that included different categories of chemical bonding. These included binding energies ranging from 1.01 to 1072.03 kJ/mol that were accurately modeled canonically to give a more unifying perspective that included diatomics CO, N_2 , H_2^+ , H_2 , HF, LiH, Mg_2 , Ca_2 , O_2 , Ar_2 , and in 1-D dissociative coordinates morphed potentials of OC-HX [X = F, Cl, Br, I], OC-HCCH, OC-HCN, OC-BrCl, and OC- Cl_2 , selected to illustrate intermolecular hydrogen and halogen bonding. The current investigation provides the fundamental physical and quantum mechanical basis to the unifying canonical approach that was used previously to describe such observations. It also correlates with the 1972 statement of J. C. Slater [20]: *there is*

*no very fundamental distinction between the van der Waals binding and covalent binding, which we have now extended to consideration of other categories of chemical bonding and to hydrogen and halogen bonding. However, most importantly, this canonical approach reflects in a stark manner the beautiful simplicity of Feynman's 1939 paper [14] and his statement that *the force on a nucleus in an atomic system is shown to be just the classical electrostatic force that would be exerted on this nucleus by other nuclei and by the electrons' charge distribution.**

Our formulations now open up entirely new ways to model aspects of chemical bonding from charge density distributions. Inherently observation-based and highly accurate, when applicable, they avoid limitations linked so often to simplifying assumptions and related uncertainties in the corresponding standard molecular quantum calculations as they do not require the determination of wave functions in multi-electron molecules and do not require consideration of electron correlation effects as they are inherent to the canonical transformation approach. One area of application that appears to have significant potential is in the development of functionals associated with DFT development though there are many others.

V. Conclusions

Canonical applications for diatomic molecules have been formulated from the perspective of the Hellmann-Feynman Theorem which is exact within the Born-Oppenheimer assumption. The role of charge density distribution in H_2^+ and H_2 have also been investigated in depth to give greater insight on these results. The corresponding canonical transformations are shown not only to have a basis in fundamental molecular quantum mechanics but their explicitly determined forms are also consistent with results of previously investigated semi-empirical studies. Most importantly, the derived canonical formulations and their correlation with charge density

distributions confirm why such applications give a unifying perspective on the origin of the nature of bonding in a wide variety of different categories of pairwise interatomic interactions and why such transformations are explicit. Moreover, the accurately calculated charge density distributions in H_2^+ and H_2 further support the conclusion that electron correlation is intrinsic to canonical transformations exclusively through the effective charge density distribution and not explicitly through the potential $V(R)$, a distinct advantage in applications of canonical approaches in chemical bonding. The currently determined results now provide the fundamental basis for generalization of corresponding formulations through application of the Hellmann-Feynman Theorem and application of the corresponding Virial Theorem to multi-dimensional polyatomic molecular systems.

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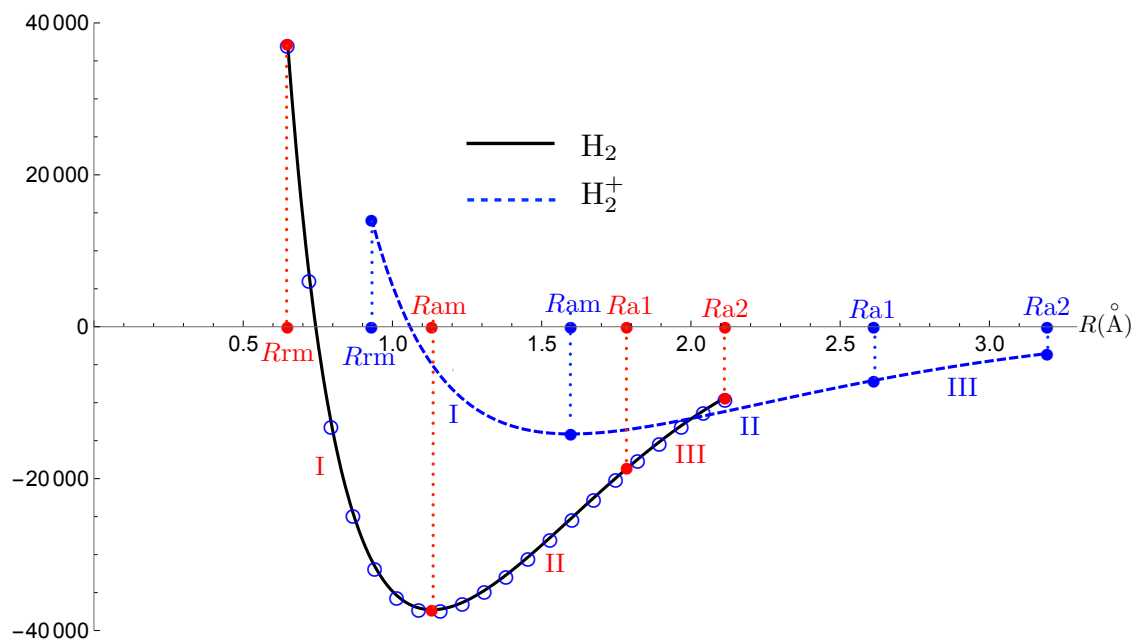


Figure 1. The Feynman force for H_2 and H_2^+ . The units of the ordinate are in $\text{cm}^{-1}/\text{Å}$.

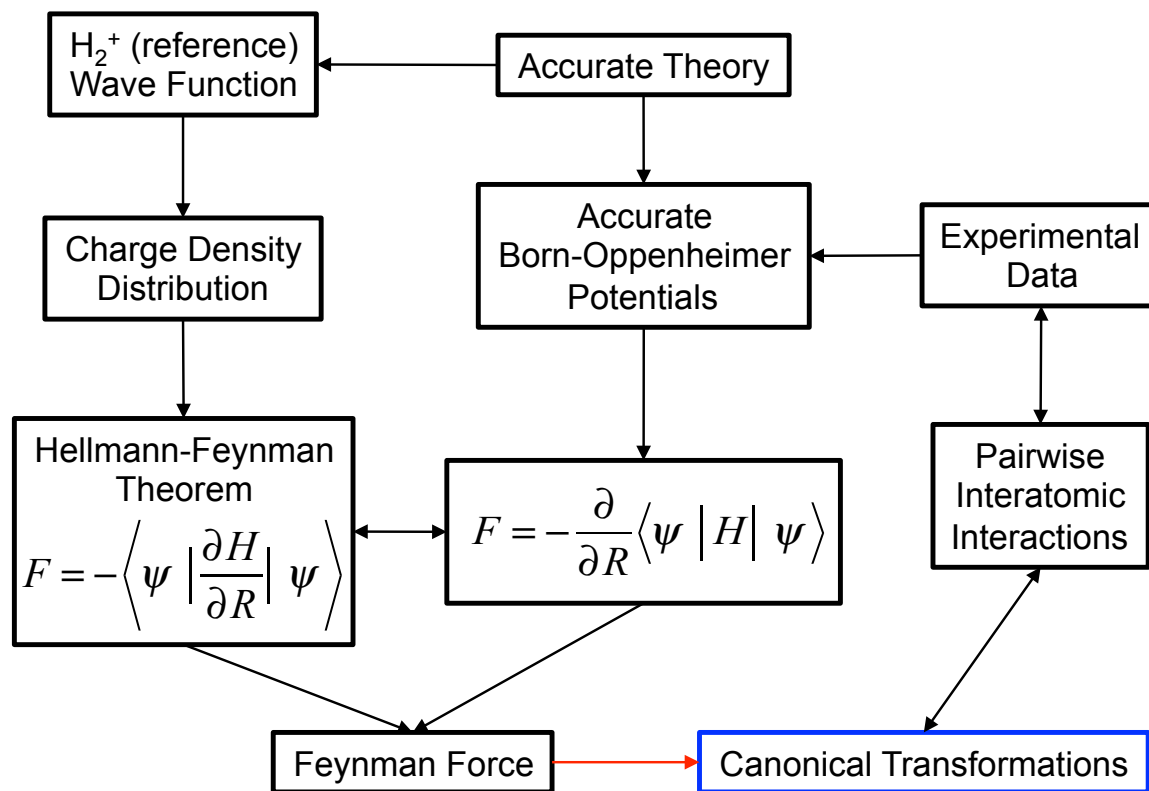


Figure 2. A block diagram illustrating the nature of the canonical transformation to the Hellmann-Feynman Theorem.

Table 1. Interatomic separations (in Å) at which the H_2^+ and H_2 charge densities were calculated.

H_2^+	H_2
0.8507	0.5898
0.8737	0.6066
0.8967	0.6235
0.9197	0.6450
0.9427	0.6600
0.9657	0.6740
0.9887	0.6909
1.0117	0.7077
1.0347	0.7246
1.0569	0.7414
1.1369	0.8104
1.2169	0.8793
1.2969	0.9483
1.3769	1.0172
1.4569	1.0862
1.5369	1.1551
1.5967	1.2241
1.6967	1.2930
1.7967	1.3620
1.8967	1.4310
1.9967	1.4999
2.0967	1.5689
2.1967	1.6378
2.2967	1.7068
2.3967	1.7757
2.4967	1.8447
2.6161	1.9136
2.7261	1.9826
2.8361	2.0515
2.9461	2.1205
3.0561	
3.2039	

Table 2. Interatomic separations (in Å) for sections I, II, III in Figure 1. The numbers in parentheses are the accurate values of R_{rm} , R_{a1} and R_{a2} for H_2^+ .

	R_1	R_2	R_3	R_4
H_2	0.649	1.133	1.786	2.116
H_2^+	0.956 (0.931)	1.599	2.43 (2.614)	3.057 (3.194)

Table 3. The relative errors between the accurate sections I, II, III of the Feynman force curve for H_2 in Figure 1 and the approximations constructed using the corresponding sections from the Feynman force curve for H_2^+ in Figure 1.

I	II	III
0.000857	0.00256	0.000941