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A General Transformation to Canonical Form for Potentials in Pairwise Interatomic Interactions

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A generalized formulation of explicit force-based transformations is introduced to investigate the concept of a canonical potential in both fundamental chemical and intermolecular bonding. Different classes of representative ground electronic state pairwise interatomic interactions are referenced to a chosen canonical potential illustrating application of such transformations. Specifically, accurately determined potentials of the diatomic molecules H_2, H_2^+, HF, LiH, argon dimer, and one-dimensional dissociative coordinates in Ar-HBr, OC-HF, and OC-Cl_2 are investigated throughout their bound potentials. Advantages of the current formulation for accurately evaluating equilibrium dissociation energies and a fundamentally different unified perspective on nature of intermolecular interactions will be emphasized. In particular, this canonical approach has significance to previous assertions that *there is no very fundamental distinction between van der Waals bonding and covalent bonding* or for that matter hydrogen and halogen bonds.

1 Introduction

A coherent representation for ubiquitous radially dependent two body pairwise interatomic interaction potentials remains elusive even in the simplest bonding.[1–3] Initially conceived Mie,[4] Lennard-Jones,[5] and Morse[6] potentials have now proliferated to over 100 different algebraic functions[7] stimulated by possible existence of a general potential function, different only for various diatomic molecules through involvement of two, three or more parameters. However, the search for a unique universal[1] or reduced[8] potential for accurately representing a wide range of such molecules continues unabated. Here, we introduce a fundamentally different approach, a generalized formulation for accurately generating explicit force-based transformations[9] to a canonical potential for both diatomic and two body intermolecular interactions. Different types of pairwise interatomic interactions in their ground electronic state are referenced to a chosen canonical potential illustrating application of such transformations. Specifically, accurately determined potentials of the diatomic molecules H_2, H_2^+, HF, LiH; Ar_2, and one-dimensional dissociative coordinates in intermolecular Ar-HBr, OC-HF, and OC-Cl_2 are selected as examples and investigated throughout their ground state bound potentials. The results indicate that an explicit transformation developed specifically for the Born-Oppenheimer potential of H_2 (ref. 10) can then be applied to

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the other selected two body molecular potentials generating a corresponding canonical potential with no adjustable parameters. Once transformed into this dimensionless form, the resulting potentials are all consistent within an absolute average accuracy of 14 parts in 10^4. The current formulation also accurately predicts equilibrium dissociation energies, D_e, for the systems investigated. Additionally, this generalized canonical approach gives a unified and fundamentally different pathway for modeling pairwise intramolecular and intermolecular interactions.

Recently, we demonstrated that different classes of ground electronic state pairwise interatomic interaction potentials could be referenced to a canonical potential[9] using a single explicit transformation generated from the extremely accurate Born-Oppenheimer potential of H_2.[10] In particular, a canonical potential and associated force distribution were constructed in the context of semi-classical Rydberg-Klein-Rees (RKR) potential methodology.[11–13] Once that explicit transformation was generated, there was no necessity for any adjustable parameters across a range of bonding types to which it was applied. A key factor in the effective application of this RKR approach was substitution of atomic instead of nuclear masses for the reduced masses in the calculations[14,15] utilized to determine the corresponding RKR potentials.[16,17] Thus partially corrected for adiabatic and non-adiabatic effects, the determined RKR potential for the interatomic interaction was closer to that within the Born-Oppenheimer approximation. A similar approach enabled generation of corresponding explicit expressions for the force distribution. Such approaches[9] were then applied to a range of diatomic molecules N_2, CO,

H_2^+, H_2, HF, LiH, Mg_2, Ca_2, O_2; argon dimer, and adapted for the intermolecular dissociative coordinates of intermolecular interactions in OC-HBr, OC-HF, OC-HCCH, OC-HCN, OC-HCl, OC-HI, OC-BrCl, and OC-Cl$_2$ one-dimensional cuts through multidimensional potentials. All respective potentials subject to transformation were consistently based on accurate semi-empirically determined interatomic RKR (ref. 16,17) or morphed intermolecular potentials.[9] This canonical approach has significance to previous assertions that *there is no very fundamental distinction between van der Waals bonding and covalent bonding*[18] or for that matter hydrogen and halogen bonds. An obvious advantage of this approach was that it was based on a reputable semi-empirical approach without necessity of specifying an algebraic form of the potential. The absolute average deviation over the systems included in such fits were 7 parts in 10,000 within applicability of the RKR method. Such approaches were, however, limited with respect to general applicability and limitations of this RKR method to cover the entire bound potentials particularly in the asymptotic limit near dissociation.

It is recognized that almost all physical phenomena, excluding the atomic nuclear structure, can be attributed directly or indirectly to the forces between atoms.[19] Knowledge of accurate interatomic potential energy surfaces are fundamental to the characterization and prediction of many properties in all states of matter whether the forces are between atoms or un-reacting molecules and fragments of molecules.[9,20–26] Molecular description of condensed phase behaviour relies on the full characterization of pairwise interactions as are properties necessary for interpretation of high resolution spectra and scattering data. Many properties of macroscopic assemblies (liquids and solids) of neutral atoms/molecules have also been derived from the Lennard-Jones (6-12) potential of two isolated atoms/molecules. Construction and optimization of empirical potentials are also important for use in Monte Carlo or molecular dynamics as well as computer simulations of bulk material.

A schematic representation of the most familiar two body interatomic potential (as initially proposed by Mie[4]) is shown in Fig. 1a. It consists of an analytical form with an attractive part at large separations approaching a minimum in the region of equilibrium separation, then becoming increasingly repulsive as R decreases further and the electron density of the two directly interacting atoms begin to overlap. Numerous mathematical models have now been developed to approximate these complicated contributions of the attractive and repulsive forces in the simplest of two body chemical and intermolecular bonding.[7] These previously described potential functions have now proliferated to analytical forms with increasing numbers of parameters and accuracy, frequently without physical significance.[2,3,6,27,28] These approaches have often provided a basis for models of pairwise interactions that

have raised issues with regard to the existence of a reduced or universal potential for diatomic molecules.[1,8] It has been expected that a universal reduced potential would not exist with any precision for all molecules in all states. However, such potentials are still and will continue to be important despite advances in quantum mechanical calculations because of their tremendous conceptual and computational simplification. Fundamental changes in our understanding of pairwise potentials as representations of the simplest chemical and non-covalent bonding thus have significant implications for modeling of innumerable phenomena in more complex environments.
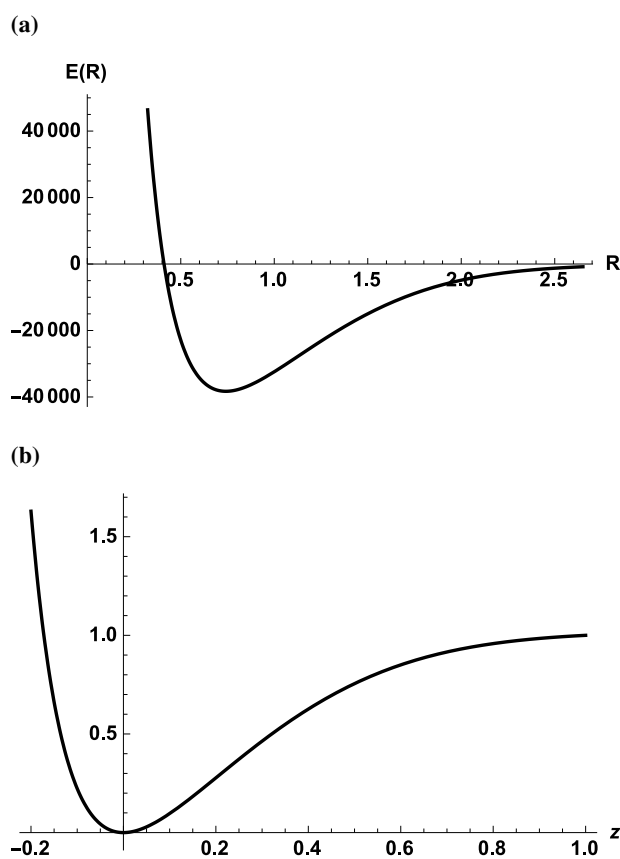
(a)

(b)

Fig. 1 (a) Dimensional (unscaled) $E(R)$ potential for H_2. Units are Å for interatomic distance and cm^{-1} for the potential energy. (b) Dimensionless (scaled) canonical potential $\tilde{E}_\alpha(z)$.

2 Methods

2.1 Potential Energy Curves and Dissociation Energies

The potential energy curves and determined equilibrium dissociation energy, D_e, for H_2 were obtained from reference 10.

The corresponding information for H_2^+, LiH, HF, and Ar_2 were available, respectively, from references 29–32. For the complexes Ar-HBr, OC-HF, and OC-Cl$_2$, a one-dimensional potential along the dissociative coordinate and the corresponding D_e were obtained from data, respectively, in references 33–35.

2.2 Family of Canonical Transformations

For subsequent demonstration, we shall first recall the classical relations[36–38] for diatomic molecules:

$$T(R) = -E(R) - RE'(R) = -E(R) + RF(R) \quad (1)$$
$$V(R) = 2E(R) + RE'(R) = 2E(R) - RF(R) \quad (2)$$

in which we make use of the force/potential relation: $F(R) = -E'(R)$. Letting R_M and F_M satisfy $F(R_M) = F_M$ where F_M denotes the maximum value of $F(R)$ for $R_e < R$ with R_e denoting the inter-nuclear separation at equilibrium.

A one parameter family of canonical transformations of $E(R)$ for $R > R_e$ (the attractive side of the potential), denoted by $\tilde{E}_\alpha(z)$ for $0 < z < 1$, was constructed by first defining R_α such that $F(R_\alpha) = \alpha F_M$, for any $0 < \alpha < 1$ and then defining:

$$\tilde{E}_\alpha(z) := \frac{E(R) - E(R_e)}{E(R_\alpha) - E(R_e)} \quad (3)$$

in which z and R are related through: $z = (R - R_e)/(R_\alpha - R_e)$. The canonical potential eqn (3) could then be readily extended to the repulsive side of the potential by taking $z < 0$.

What must be demonstrated for eqn (3) to be called *canonical* is that given two different potentials $E^j(R)$, for $j = 1, 2$, where $\tilde{E}_\alpha^1(z) = \tilde{E}_\alpha^2(z)$ for $z_- < z \le 0$ and $0 \le z < 1$ for fixed, chosen $0 < \alpha < 1$ and a common value of z_- (defined by the portion of the repulsive-side of the potentials represented in the canonical scaling).

2.3 Reverse Canonical Transformation

The transformation inverse to eqn (3) gave the canonical representation of $E(R)$:

$$E(R) = E(R_e) + (E(R_\alpha) - E(R_e))\tilde{E}_\alpha(z) \quad (4)$$

for $R_e < R < R_\alpha$, and z is given above.

2.4 Implications Derived from the Canonical Transformation

From eqn (4) it followed that: $F(R) = \bar{F}_\alpha \tilde{E}_\alpha'(z)$, in which $\bar{F}_\alpha$ denoted the *Average Force* over the interval $R_e < R < R_\alpha$ defined by:

$$\bar{F}_\alpha := \frac{1}{R_\alpha - R_e} \int_{R_e}^{R_\alpha} F(R)\,dR = -\frac{E(R_\alpha) - E(R_e)}{R_\alpha - R_e}. \quad (5)$$

Evaluating eqn (5) at $R = R_M$ give the important relation:

$$F_M = \left(\frac{\tilde{E}_\alpha'(1)}{\alpha}\right)\bar{F}_\alpha. \quad (6)$$

Eqn (6) implying that the ratio of the maximum force to the average force was the same for all diatomic molecules in the class for which the canonical transformation eqn (4) held. Combining eqn (1) and (4) gave the canonical representation for $T(R)$:

$$T(R) = E(R_e) - (E(R_\alpha) - E(R_e))\tilde{E}_\alpha(z)$$
$$- (R_e + z(R_\alpha - R_e))\bar{F}_\alpha\tilde{E}_\alpha'(z). \quad (7)$$

2.5 Generalized Canonical Transformation

The canonical transformation eqn (3) was generalized to extend its range of validity $0 < \alpha_0 < \alpha < 1$ to smaller values of α_0. One such generalization was defined by:

$$\tilde{E}_\alpha(z;\gamma) := \frac{E(z\gamma R_\alpha + (1 - z\gamma)R_e) - E(R_e)}{E(R_\alpha + (\gamma - 1)(R_\alpha - R_e)) - E(R_e)} \quad (8)$$

where $0 < \gamma$. Clearly, eqn (8) reduces to eqn (3) for $\gamma = 1$.

2.6 Reverse Generalized Transformation

The transformation inverse to eqn (8) gave:

$$E(R) = E(R_e) + (E(R_\alpha + (\gamma - 1)(R_\alpha - R_e)) - E(R_e))$$
$$\times \tilde{E}_\alpha\left(\frac{1}{\gamma}\left(\frac{R - R_e}{R_\alpha - R_e}\right);\gamma\right) \quad (9)$$

$$F(R) = -\frac{(E(R_\alpha + (\gamma - 1)(R_\alpha - R_e)) - E(R_e))}{\gamma(R_\alpha - R_e)}$$
$$\times \tilde{E}_\alpha'\left(\frac{1}{\gamma}\left(\frac{R - R_e}{R_\alpha - R_e}\right);\gamma\right). \quad (10)$$

2.7 Dyadic Generalized Canonical Force Transformation

A canonical force transformation was derived for $R > R_e$ by making use of the *dyadic* sequence $\{R_0, R_1, \ldots\}$ defined by: $R_0 := R_m$ and for $j = 1, 2, \ldots,$

$$F(R_j) = \frac{F_m}{2^j} \quad (11)$$

where $F_m = F(R_m)$ is the maximum value of $F(R)$ for $R > R_e$. Then for $j \ge 1$ and $R_{j-1} \le R \le R_j$:

$$\tilde{F}_j(z) := \frac{F(zR_j + (1 - z)R_{j-1}) - F(R_{j-1})}{F(R_j) - F(R_{j-1})} \quad (12)$$

was defined for $0 \le z \le 1$. From eqn (11) and (12) it followed immediately that:

$$\tilde{F}_j(z) := 2 - \frac{2^j F(zR_j + (1 - z)R_{j-1})}{F_m}. \quad (13)$$

The reverse transformation corresponding to eqn (13) took the form:

$$F(R) = \frac{F_m}{2^j}\left(2 - \tilde{F}_j\left(\frac{R - R_{j-1}}{R_j - R_{j-1}}\right)\right),$$
$$\text{for} \quad R_{j-1} \leq R \leq R_j. \quad (14)$$

For $R_e \leq R \leq R_0$, eqn (13) and (14) take the form:

$$\tilde{F}_0(z) := \frac{F(zR_0 + (1-z)R_e)}{F_m}, \quad \text{for} \quad 0 \leq z \leq l \quad (15)$$

$$F(R) = F_m\tilde{F}_0\left(\frac{R - R_e}{R_0 - R_e}\right). \quad (16)$$

2.8 Power-Law Distribution

When $R_{j-1} < R < R_j$, $F(R)$ had the simple power-law form:

$$F(R) = \frac{A_j}{R^{N_j}} \quad (17)$$

which with the requirement, $F(R_{j-1}) = (F_m)/(2^{j-1})$, implies that eqn (17) took the form:

$$F(R) = \frac{F_m}{2^{j-1}}\left(\frac{R_{j-1}}{R}\right)^{N_j}. \quad (18)$$

When the additional condition, $F(R_j) = (F_m)/(2^j)$, was imposed yielded the relation:

$$N_j = \frac{\log(2)}{\log(R_j/R_{j-1})}. \quad (19)$$

Hence, given R_j and R_{j-1}, N_j was determined from eqn (19).

2.9 Application to Estimating D_e

Estimations for D_e where evaluated from the Dyadic Canonical Force Transformation eqn (12) and the usual relationship: $D_e = \int_{R_e}^{\infty} F(R)dR$. Expanding this relationship and appealing to eqn (13) - (18):

$$D_e = \int_{R_e}^{R_m} F(R)dR + \sum_{j=1}^{k}\int_{R_{j-1}}^{R_j} F(R)dR$$
$$+ \int_{R_k}^{\infty} F(R)dR \quad (20)$$

$$\approx F_m\left[(R_m - R_e)\hat{F}_0 + \sum_{j=1}^{k}\frac{(R_j - R_{j-1})}{2^j}(2 - \hat{F}_j)\right.$$
$$\left. + \frac{R_k(R_{k-1}/R_k)^{N_k}}{(N_k - 1)2^{k-1}}\right] \quad (21)$$

was derived where

$$\hat{F}_j := \int_0^1 \tilde{F}_j(z)dz, \quad \text{for} \quad j = 0, 1, \ldots. \quad (22)$$

The last term in eqn (21) assumed that the power-law behavior eqn (17) gave a good approximation to the tail distribution of the force $F(R)$ for $R > R_{k-1}$ and then integrating eqn (18) over the interval $R_k < R < \infty$. The exponent N_k in eqn (21) was determined from eqn (19) with $j = k$. The numbers $\hat{F}_j$ in eqn (21) were canonical in that they are computed from the canonical force distribution $\tilde{F}_j(z)$ through eqn (22). In the applications below, the canonical parameters $\hat{F}_j$ were computed from the force distribution corresponding to H_2 and used to estimate the dissociation energy D_e for all other molecules considered. The values of $\hat{F}_j$ are 0.734, 0.420, 0.535, 0.547, 0.553, 0.557, 0.557, 0.568, and 0.562; respectively for $j = 0, \ldots, 8$. It was noted that the canonical parameters $\hat{F}_j$ were quite close in value for $j = 2, \ldots, 8$ reflective of the fact that the dyadic canonical force distributions $\tilde{F}_j(z)$ were nearly identical curves for $0 \leq z \leq 1$ indicative of the highly regular pattern by which the force was reduced from its maximum modulus by increasing factors of $1/2$. Indeed, in estimation of D_e for the class of molecules discussed below, the canonical values $\hat{F}_j$ for $j = 2, \ldots, 8$ was replaced by their average at the cost of a very small additional error.

3 Results and discussion

In order to demonstrate a general canonical transformation in pairwise interatomic interactions, we will first formulate an explicit force-based approach that maps potentials to their canonical form and to their corresponding force distributions. Construction of this canonical dimensionless potential from pairwise interatomic potentials in a wide class of diatomic molecules is enabled via an explicitly defined scaling transformation, guided by the associated force distribution. These involve the derivation of eqn (3) and (8). Figure 1a shows the dimensional unscaled potential curve for H_2. The corresponding dimensionless scaled canonical potential calculated from equation (3) is given in Fig. 1b.

As discussed above, eqn (3) or the more general eqn (8) are to be viewed as a *canonical* potential for a class of molecules. However, it must be demonstrated that for given $0 < \alpha < 1$, eqn (3) or (8) are constructed for any pair of molecules within the chosen class to agree within an acceptable level of accuracy. Figure 2 shows the dimensionless potential $\tilde{E}_4(z;\gamma)$ constructed up to R_4 (the point where the maximum attractive force of each molecule is reduced by a factor of $1/16$) for strongly bound (Fig. 2a) and weakly bound (Fig. 2b) interatomic interactions. For each system, the parameter γ is interpolated at the point $z = 0.5$ to select the precise portions of the unscaled potential curves identified in the dimensionaless scaling. The relative error in the canonical potential and force curves was calculated for the studied species relative to the H_2 molecule. The relative error between two functions on the interval (a,b) is given by $\int_a^b |f(x) - g(x)|dr/\int_a^b |g(x)|dx$. The
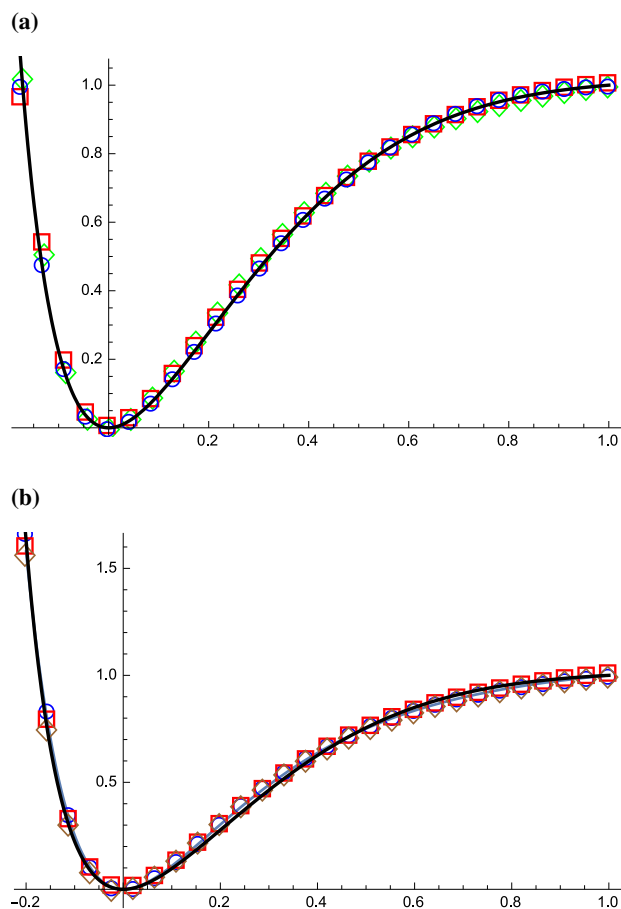
(a)

(b)

Fig. 2 (a) Dimensionless potential $\tilde{E}_4(z;\gamma)$ for: H_2 (solid curve), HF ($\square$), H_2^+ ($\diamondsuit$), and LiH ($\bigcirc$). (b) Dimensionless potential $\tilde{E}_4(z;\gamma)$ for: H_2 (solid curve), Ar_2 ($\triangle$), OC-HF ($\square$), OC-Cl_2 ($\bigcirc$), and Ar-HBr ($\diamondsuit$).

average absolute error in the canonical potential is 14 parts in 10^4 over the range of experimentally available data, which is approximately twice the value for the corresponding RKR approach.[9] This is not unexpected as determination of the force from the RKR potential is explicit, whereas the current case involves direct determination of the gradient.

We emphasize that the canonical transformation eqn (3) is based upon a remarkably simple construction. Indeed, eqn (3) is an elementary affine transformation of the portion of the dimensional potential curve $E(R)$ between R_e and R to a dimensionless counterpart. The challenge required to make this process *canonical* is to identify the portions of the dimensional potential curves for a large class of molecules that transform to coincident dimensionless counterparts via this affine. The key to identifying these canonical portions of the dimensional potential curves is held by the associated dimensional

force distributions. More specifically, if F_m is the maximum (in absolute value) of the force for $R_e < R$, then canonical portions of dimensional potential curves are defined by $R_e < \hat{R}$ where $F(\hat{R})/F_m$ is constant across molecules in the chosen class. This is a most important issue in this current work as it is the force that selects canonical portions of potential curves.

An important consequence of the canonical transformation appears in eqn (6), implying that the ratio of the maximum force to the average force is the same for all diatomic molecules in the class for which the canonical transformation holds.

Further applications of this generalized canonical approach involve the power-law distribution of the maximum attractive force that permits estimation of D_e in the systems studied. Figure 3 shows a plot of the unscaled force curve for H_2 molecule. The equilibrium bond length, R_e, which occurs when the force is zero, is indicated with the black dotted line. The maximum attractive force, $-|F_m|$, located at R_m is represented with the red dotted lines. The blue, green, orange, and brown dotted lines locates, respectively, the position R_j (j = 1,2,3,4) where the maximum force is reduce by a factor of 2^{-j}. Table 1 gives the prediction of D_e for the studied molecules and the % error relative to accurately known values. As shown in Table 1, all predictions deviate less than 0.5%. Whether the source of this residue error lies fundamentally in the model, in the accuracy of experimentally determined frequencies including neglect of non-Born-Oppeheimer corrections or computational inaccuracies has yet to be evaluated. Moreover, once the explicit transformation is determined for the reference molecule, H_2, no adjustable parameters are needed for predicting the presented data for the other systems in Table 1. It is pertinent to note that an error of 0.5% or less in the weakly bound complexes D_e is comparable to the best experimental determinations.
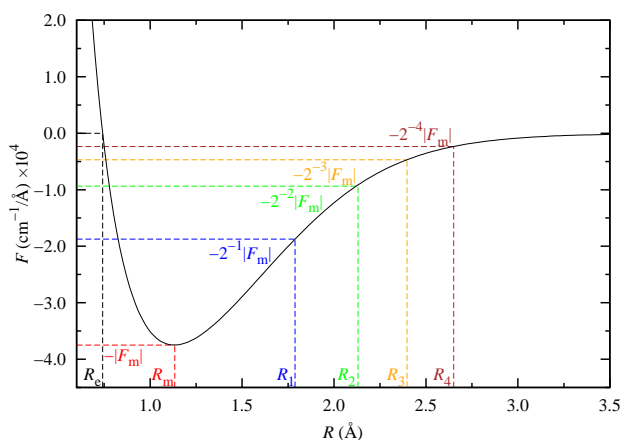

Fig. 3 Unscaled force curve for H_2, illustrating the power-law distribution of the maximum attractive force, F_m.

Table 1 Prediction of the dissociation energies, D_e, for the studied molecules.

	H_2	H_2^+	LiH	HF	Ar_2	Ar-HBr	OC-HF	OC-Cl$_2$
D_e (cm^{-1}) true	38293.017	22532.1	20286.8	49361.6	99.5	175.99	1309.65	544.2
D_e (cm^{-1}) est	38322.8	22576.5	20306.5	49250.0	99.46	175.83	1313.78	546.8
% error	0.08	0.20	0.10	-0.23	-0.04	-0.09	0.32	0.48
R_e (Å)	0.7414	1.0582	1.595	0.917	3.761	4.247	3.598	4.741
F_m (cm^{-1}/Å)	37484.92	14266.71	11824.4	54453.9	80.32	133.8	975.92	397.44
R_m (Å)	1.134	1.599	2.259	1.246	4.166	4.632	3.998	5.233
R_1 (Å)	1.788	2.595	3.426	1.852	4.882	5.432	4.793	5.959
R_2 (Å)	2.121	3.201	3.997	2.192	5.388	5.967	5.319	6.523
R_3 (Å)	2.397	3.741	4.375	2.437	5.915	6.54	5.894	7.121
R_4 (Å)	2.651	4.237	4.625	2.607	6.469	7.104	6.545	7.837
R_5 (Å)	2.893	4.693	4.783		7.11		7.355	8.449
R_6 (Å)	3.132				7.793		8.263	9.189
R_7 (Å)							9.271	

4 Conclusions

We have demonstrated for the selected molecules that there is a transformation to a canonical potential with an absolute error of 14 parts in 10^4, throughout the range of experimentally determined bound potentials and with no adjustable parameters. The development of the power-law distribution provides a new approach to estimating equilibrium dissociation energies that should prove particularly effective for weakly bound interactions. The concept of the derived canonical approach should provide the basis for extensive modeling of pairwise interactions and for widespread applications in more complex systems with larger vibrational dimensions.

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