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PAPER

View Article Online
View Journal | View Issue

Cite this: Phys. Chem. Chem. Phys., 2017, 19, 15864

Is there any fundamental difference between ionic, covalent, and others types of bond? A canonical perspective on the question

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Received 13th April 2017,
Accepted 26th May 2017

DOI: 10.1039/c7cp02407j

rsc.li/pccp

The concept of chemical bonding is normally presented and simplified through two models: the covalent bond and the ionic bond. Expansion of the ideal covalent and ionic models leads chemists to the concepts of electronegativity and polarizability, and thus to the classification of polar and non-polar bonds. In addition, the intermolecular interactions are normally viewed as physical phenomena without direct correlation to the chemical bond in any simplistic model. Contrary to these traditional concepts of chemical bonding, recently developed canonical approaches demonstrate a unified perspective on the nature of binding in pairwise interatomic interactions. This new canonical model, which is a force-based approach with a basis in fundamental molecular quantum mechanics, confirms much earlier assertions that in fact there are no fundamental distinctions among covalent bonds, ionic bonds, and intermolecular interactions including the hydrogen bond, the halogen bond, and van der Waals interactions.

1. Introduction

The chemical bond is one of the most fundamental concepts in chemistry taught to students in general chemistry courses even at the high school level. It is common to first teach students that the chemical bond consists of two extreme models: the covalent bond model and the ionic bond model. The covalent bond is described as a sharing of electrons; the ionic bond is described as a consequence of Coulombic attractions between opposite charges on the interacting atoms. These simplistic models are further refined by introducing the concepts of electronegativity and polarizability effects which lead to the classification of polar and non-polar bonds. The concept of intermolecular interaction, such as the hydrogen bond and van der Waals interactions, are normally viewed as physical phenomena with no direct correlation to the chemical bond. Intermolecular interactions are described as electrostatic, dispersion, and polarization effects between pairs of atoms or molecules.

However, in his classic book, The Nature of the Chemical Bond, L. Pauling defined the chemical bond as follows:[1] "*We shall say that there is a chemical bond between two atoms or groups of atoms in case that the forces acting between them are such as to lead to the formation of an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species.*" This definition makes no distinction between a covalent or ionic bond, and states that it is the force acting between atoms or group of atoms that is responsible for binding.

Then, in 1972 J. C. Slater made the controversial statement:[2] "*The writer believes that there is no very fundamental distinction between the van der Waals binding and covalent binding.*" This contention suggests that covalent bonds, ionic bonds, hydrogen bonds, halogen bonds, and van der Waals interactions are indeed fundamentally the same. In particular, Slater's assertion suggests that there is not a fundamental difference between the very weak van der Waals bond of argon dimer, say, and the strong triple covalent bond of carbon monoxide even though these two molecules have three orders of magnitude difference in their bond strength, 1.02 kJ mol^{-1} for argon dimer and 1071.52 kJ mol^{-1} for CO. The idea that binding in these two systems have the same fundamental intrinsic nature is controversial. The nature of the chemical bond is still an oft-debated subject.[3–6] It is not within the scope of this work to enter into the binding controversy, but rather to describe a new point of view on molecular potentials and forces that might prove useful in discussions of binding. The central goal of the present contribution is to offer a perspective on binding that supports Slater's assertion. In particular, we shall show from this perspective a sense in which argon dimer could be viewed as a diatomic molecule.

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2. Potential energy functions

Empirical algebraic potential energy functions continue to play a prominent role in modeling pairwise interatomic interactions.[7–9] Over 100 of those functions have now been proposed,[10] involving from two to significantly larger numbers of adjustable parameters. Considerable effort has gone into enhancing the effectiveness of the algebraic potential energy functions that have the minimum number of adjustable parameters and still have the most widespread applicability and predictability.[11,12] Several studies have also focused on the determination of universal and reduced potentials[10,13] with the objective of finding a fundamentally unifying approach to understanding interatomic interactions. There have also been studies that show a connection among the parameters of the generalized version of the Morse, Lennard-Jones, Rydberg, and Buckingham potentials functions.[14,15] The Morse[16,17] potential, a three-parameter model, has shown continued popularity for widespread applications in describing pairwise interatomic covalent bonding. It had been shown that many hydrogen- and halogen-bonded complexes have binding energies directly proportional to the intermolecular stretching force constant and that both could therefore reasonably be described by the Morse potential.[18] The Lennard-Jones[19,20] potential which can be regarded as a special case of the Mie potential,[21] is the common choice for describing intermolecular interactions (such as van der Waals interactions, hydrogen bonding, and halogen bonding). The Lennard-Jones function offers computational advantages over other functions and it has only two adjustable parameters.

One of the most elegant methods for determining accurate potential curves for diatomic molecules is the semi-classical Rydberg–Klein–Rees (RKR) procedure and its variants.[22–27] Previously, a canonical potential and a canonical force were constructed in the context of semi-classical RKR potential methodology.[28] The terms canonical potential and canonical force refer to dimensionless functions obtained from each molecule within the defined class by a readily invertible algebraic transformation. Furthermore, to be deemed canonical, the dimensionless potentials or forces obtained from all of the molecules within the defined class by the canonical transformation must agree to within a specified order of high accuracy. 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; which include the diatomic molecules N_2, CO, H_2^+, H_2, HF, LiH, Mg_2, Ca_2, O_2; argon dimer, and one-dimensional cuts through the intermolecular dissociative coordinates in the multidimensional potentials of the intermolecular interactions in OC–HBr, OC–HF, OC–HCCH, OC–HCN, OC–HCl, OC–HI, OC–BrCl, and OC–Cl_2. Such approaches were, however, limited with respect to general applicability and the limitations of the RKR method to cover the entire bound potentials particularly in the asymptotic limit near dissociation.

In a recent work[29] canonical approaches were applied to classic Morse, Lennard-Jones, and Kratzer potentials. It was found that from the canonical transformation generated for the Morse or Lennard-Jones or Kratzer potentials as a reference, inverse transformations allow the accurate generation of the Born–Oppenheimer potential for H_2^+ ion, neutral covalently bound H_2, van der Waals bound Ar_2, and the hydrogen bonded one dimensional dissociative coordinate in water dimer. In addition an algorithmic strategy based upon a canonical transformation to dimensionless form applied to the force distribution associated to a potential was developed. This algorithm lead to accurate approximations to both the force and potential functions corresponding to a particular diatomic molecule in terms of the force distribution associated with an algebraic potential energy function, such as the Lennard-Jones function.†

Classical algebraic potential energy functions try to represent the potential curve of a real molecule by involving a number of adjustable parameters that ultimately bring error to the calculations. In contrast, by using the canonical approach to algebraic potential energy functions more accurate representations of the potential curve of a real molecule are obtained, where the value of the adjustable parameters have no effect on the calculation.[29] Thus, is it necessary to have over 100 empirical algebraic potential energy functions to describe pairwise interatomic interactions, and therefore invoke different types of chemical bonding? Is there really a difference in the potential energy functions between pairwise interatomic interactions? Can a generic potential function be found that would describe this wide range of interactions? In the next section, canonical forms are derived to present a perspective on the unification of pairwise interatomic interactions, and thus provide an answer to the previous questions.

We describe here a unifying principle for understanding pairwise interatomic interactions from the perspective of recently developed, force based, canonical approaches.[28–36] The key ideas will be introduced through the consideration of pairwise interatomic interactions from the point of view of force, echoing the seminal result of R. P. Feynman[37] that "*…the force on a nucleus in an atomic system is… just the classical electrostatic force that would be exerted on this nucleus by other nuclei and by the electrons' charge distribution*". In the next section, we develop Feynman's idea into a new canonical model that unifies pairwise interatomic interactions and lends strong support to the previous assertions made by Slater.

3. Canonical forms and the unification of pairwise interatomic interactions

Recently, we introduced explicit force-based transformations to canonical forms for potentials corresponding to both diatomic and two body intermolecular interactions.[28–36] The term

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† At the suggestion of referees, the algorithms developed in ref. 29 were applied to the very weakly-bound helium dimer. In particular, employing the canonical and inverse-canonical transforms with the Lennard-Jones 6-12 potential as reference, the He_2 potential was approximated over the range $R_{r8} < R < R_2$ (R_{r8} = 1.991 Å, R_2 = 4.283 Å, and R_e = 2.968 Å) with a relative error of 0.00586. The relative error is defined by $\int_{R_{r8}}^{R_2} \left|E(R) - \tilde{E}(R)\right| \mathrm{d}R \Big/ \int_{R_{r8}}^{R_2} |E(R)| \mathrm{d}R$. In this definition, $E(R)$ is the accurate potential and $\tilde{E}(\mathrm{R})$ is the canonical approximation to the He dimer potential. The accurate potential was taken to be the Born–Oppenheimer potential of Jeziorska *et al.*, *J. Chem. Phys.*, 2007, **127**, 124303. The details are beyond the scope of the present contribution and will appear in a forthcoming paper.

canonical form for a class of molecular potentials refers to a dimensionless function obtained from each molecular potential within the defined class by a readily invertible piecewise affine (a function that performs a uniform scaling and translation of one interval of real numbers onto another interval) transformation. Furthermore, to be deemed canonical, the dimensionless forms obtained from all of the molecular potentials within the defined class by the canonical transformation must agree to within a specified order of high accuracy. The salient feature of these canonical forms is that they encode the "shape" of their associated molecular potential curves. The above definition of canonical form implies that the potential curves for all of the molecules in the considered class that share a common canonical form have the same shape. Just what this means is explained below. We note also that it has been shown[36] that the origin of these canonical transformations is rooted in the Hellmann–Feynman theorem[37,38] and thus to fundamental molecular quantum mechanics.

The key tool for constructing the canonical transformation is the Feynman force.[37] This is a virtual force arising from a thought experiment, which is most easily visualized in the setting of a diatomic molecule. For illustrative purposes, consider the diatomic molecule H_2. The thought experiment consists of defining $E(R)$ to be the static (ground electronic state) energy of the H_2 molecule when the two nuclei are separated a distance R. This energy is calculated by solving the static (time independent) Schrödinger equation with the nuclei held at the fixed separation distance R (*i.e.*, the Born–Oppenheimer approximation[39]). The Feynman (virtual) force is defined by: $F(R) = -E'(R)$, that is, the negative of the derivative of the potential $E(R)$ with respect to the separation distance R. This idea is readily generalized to any diatomic molecule and, indeed, to any molecule irrespective of the number of nuclei. Fig. 1a and b show graphs of $E(R)$ and $F(R)$ for H_2 and the diatomic ion H_2^+. One should notice that in Fig. 1a and b, R_e denotes the equilibrium nuclear separation distance at which the force vanishes ($F(R_e) = 0$) and the potential attains its minimum value $-D_e$ where D_e is the dissociation energy of the molecule, *i.e.*, the energy required to break the diatomic molecule into two separate atoms. When the separation distance $R > R_e$, the force is attractive (binding) while when $0 < R < R_e$ the force is repulsive (anti-binding). Also, the value of $F(R)$ (considering the nuclei as point charges) goes to infinity as R approach zero and $F(R)$ goes to zero as R approach infinity.

In Fig. 1a, S_0 denotes the section of the potential curve $E(R)$ for $R_e \leq R \leq R_m$ which, as seen in Fig. 1b, corresponds to the section of the force curve $F(R)$ on which the force goes from zero to its maximum attractive magnitude F_m. A key observation is that the S_0 section for H_2 (red) and for H_2^+ (blue) have the same shape, where the shape of S_0 is defined through the canonical transformation to dimensionless form:

$$c_{\mathrm{em}}(x) = \frac{E(xR_{\mathrm{m}} + (1-x)R_{\mathrm{e}}) - E(R_{\mathrm{e}})}{E(R_{\mathrm{m}}) - E(R_{\mathrm{e}})}, \quad \text{for} \quad 0 \leq x \leq 1. \tag{1}$$

Fig. 2 shows the canonical form $c_{\mathrm{em}}(x)$ for H_2 (solid red curve) and H_2^+ (blue circles). The two curves have a relative error of 0.0026. The canonical form $c_{\mathrm{em}}(x)$ results from an affine scaling of the potential curve $E(R)$ for $R_e \leq R \leq R_m$ to dimensionless form and reflects the inherent shape of the dimensional curve $E(R)$. Two curves will be declared to have the same inherent shape if their associated canonical forms agree to within a specified error tolerance.

In similar fashion, the section S_1 for H_2 and H_2^+ in Fig. 1a, defined for $R_m \leq R \leq R_1$, are also seen to have the same inherent shape where the associated canonical form is defined by:

$$c_{\mathrm{m1}}(x) = \frac{E(xR_1 + (1-x)R_{\mathrm{m}}) - E(R_{\mathrm{m}})}{E(R_1) - E(R_{\mathrm{m}})}, \quad \text{for} \quad 0 \leq x \leq 1. \tag{2}$$

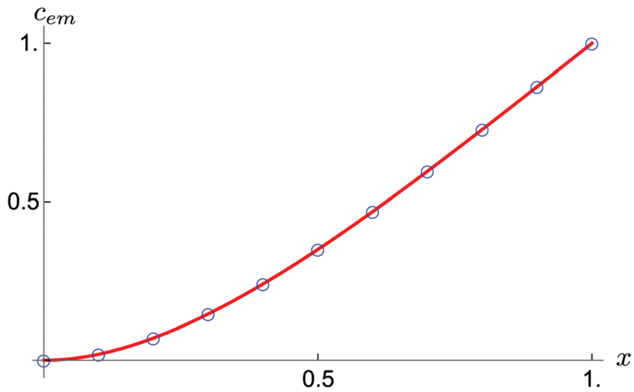

Fig. 2 Canonical potential curve $c_{\mathrm{em}}(x)$ for H_2 (solid red curve) and H_2^+ (blue circles).

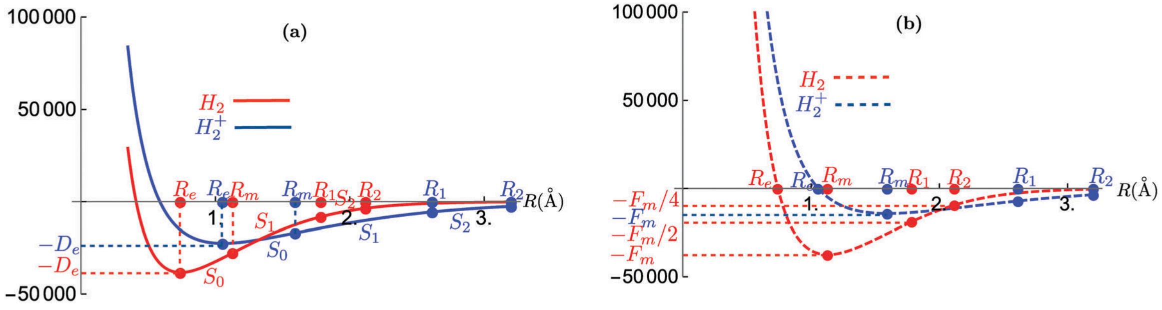

Fig. 1 Potential, $E(R)$, and Force, $F(R)$, curves for H_2 and H_2^+. Panel (a) graphs of $E(R)$ in cm^{-1} for H_2 (red) and H_2^+ (blue). Panel (b) graphs of $F(R)$ in cm^{-1} Å^{-1} for H_2 (red) and H_2^+ (blue).

The right-endpoint of the section S_1 is R_1 which, as shown in Fig. 1b, is defined by the requirement that the force $F(R_1) = -F_m/2$, that is, R_1 is the nuclear separation distance at which the attractive force has been reduced to half its maximum magnitude F_m. The canonical forms in eqn (2) for H_2 and H_2^+ agree to a relative error of 0.0022.

The section S_2 for H_2 and H_2^+ in Fig. 1a, defined for $R_1 \le R \le R_2$, have the same inherent shape with associated canonical form defined by:

$$c_{12}(x) = \frac{E(xR_2 + (1-x)R_1) - E(R_1)}{E(R_2) - E(R_1)}, \quad \text{for} \quad 0 \le x \le 1. \qquad (3)$$

The right-endpoint of the S_2 is R_2 defined in Fig. 1b by $F(R_2) = -F_m/4$, that is, the internuclear separation for which the attractive force has been reduced to one-quarter of its maximum magnitude. The canonical form in eqn (3) for H_2 and H_2^+ agree up to a relative error of 0.00042.

More generally, we define the sections S_j of the potential curves in Fig. 1a by $R_{j-1} \le R \le R_j$ where the separation distances R_j are defined by $F(R_j) = -F_m/2^j$, and the associated canonical dimensionless form:

$$c_{(j-1)j}(x) = \frac{E\left(xR_j + (1-x)R_{j-1}\right) - E\left(R_{j-1}\right)}{E\left(R_j\right) - E\left(R_{j-1}\right)}, \quad \text{for} \quad 0 \le x \le 1. \qquad (4)$$

Each of the sections S_j for H_2 and H_2^+ for $j = 0, 1, 2,\ldots$ have the same inherent shape. Moreover, it is the associated force curves that carry this inherent shape information in that the force determines the endpoints of the various sections S_j.

Similar constructions can be carried out on the repulsive side of the potential, that is, $0 < R \le R_e$, only now one defines the sequence of section endpoints $\ldots R_{rj} < R_{r(j-1)} < \cdots < R_{r1} < R_{r0} < R_e$ by $F(R_{rj}) = F_m 2^j$. In particular, R_{r0} is the internuclear separation at which the repulsive force has magnitude equal to F_m, the maximum value of the attractive force. At successive values R_{rj}, the repulsive force doubles. The sections S_{rj} of the potential curves for H_2 and H_2^+ between corresponding endpoints R_{rj} and $R_{r(j-1)}$ have the same inherent shape. The definition of the endpoints R_j and R_{rj} as explained above is not unique and indeed it can be generalized as reported previously.[34,35]

It should be emphasized that H_2 and H_2^+ are two-electron and one-electron molecules, respectively, yet their repulsive walls can be decomposed into sections of the same inherent shape. It follows that electron–electron repulsion must play only a very minor role in determining the inherent shape of the potential curve since for the ion H_2^+, there is no electron–electron repulsion.

This construction of sections of potential curves *via* their associated force curves has been applied to a wide variety of weakly and strongly bound diatomic molecules and intermolecular complexes. Fig. 3 show on the left a plot of the dimensional potential energy curves of weakly bound molecules (red; (i) Ar_2 (ii) Ar–HBr (iii) OC–Cl_2 (iv) OC–HF) and strongly bound molecules (blue; (i) H_2 (ii) H_2^+ (iii) LiH (iv) CO). Note that these molecules have been deliberately chosen to furnish examples of (i) a van der Waals molecule, (ii) a weak hydrogen-bonded molecule, (iii) a halogen-bonded molecule, (iv) a stronger hydrogen bond than in (ii), (v) the classic two-electron covalent bond, (vi) the classic one-electron bond, (vii) an ionic bond, and (viii) a covalent multiple bond. Different characteristics of these dimensional potential energy curves reflect the different types and classes of interatomic binding represented. However, applying the canonical transformation to dimensionless form to the sections of the potential curves discussed above for each of the molecules, reveals that these dimensional potential energy curves all have the same inherent dimensionless shape. The fact that each of the potential energy curves in Fig. 3 can be transformed to the same dimensionless canonical curve *via* a piecewise affine transformation suggests that the intrinsic binding characteristics inherent in covalent bonds, ionic bonds, and intermolecular interactions yield associated force distributions that share a common dimensionless shape. Therefore, what emerges from the canonical transformation is that the potential energy curve associated

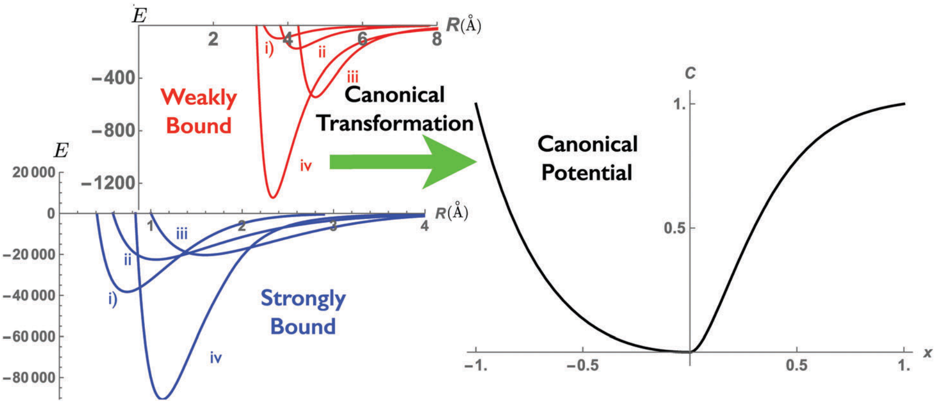

Fig. 3 Weakly bound (red; (i) Ar_2 (ii) Ar–HBr (iii) OC–Cl_2 (iv) OC–HF) and strongly bound (blue; (i) H_2 (ii) H_2^+ (iii) LiH (iv) CO) pairwise interatomic interactions potential energy curves ($E(R)$ in cm^{-1}) transformed to one canonical potential curve. On the attractive side, for each molecule, the canonical transformation is applied from the equilibrium interatomic separation to the point where the force is reduced to $F_m/2$. On the repulsive side, for each molecule, the canonical transformation is applied from the equilibrium interatomic separation to the point where the force is $2F_m$. On the attractive side the canonical potential is evaluated at x, $0 \le x \le 1$, whereas on the repulsive side the canonical potential is evaluated at $-x$, $-1 \le x \le 0$.

with two body pairwise interatomic interactions have the same shape that gets revealed from their dimensionless canonical forms. In particular, what appear to be different shapes in the potential curves in Fig. 3 for different pairwise interatomic interactions is really a matter of scaling. This scaling becomes transparent through the dimensionless canonical transformations described above. These results demonstrate, for example, that there is not a fundamental difference in the binding between argon dimer and carbon monoxide, supporting the previous assertion by Slater and giving a unification of pairwise interatomic interactions. In addition, within the canonical model, the argon dimer is considered as a diatomic molecule.

4. Conclusions

Recently developed canonical approaches to understanding molecular and intermolecular potentials and forces demonstrate "*...that there is no very fundamental distinction between van der Waals binding and covalent binding*",[2] or by extension, between covalent and hydrogen or halogen binding.[28–36] These observations based upon shape-revealing, canonical transformation of potentials and their associated force distributions to dimensionless canonical forms provide compelling arguments in support of Slater's brilliant insight. Perhaps, this new canonical perspective on interatomic interactions provide a framework with which, it should be argued that, as asserted by Slater, pairwise interatomic interactions are fundamentally the same.

Acknowledgements

We give special thanks to the Laboratory for Molecular Simulation, the High Performance Research Computing, and the Institute for Applied Mathematics and Computational Science at Texas A&M University. The authors also thank Anthony C. Legon for useful discussions.

References

1 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, 3rd edn, 1960, ch. 1, p. 6.
2 J. C. Slater, Hellmann–Feynman and Virial Theorems in the $X\alpha$ Method, *J. Chem. Phys.*, 1972, **57**, 2389–2396.
3 R. F. W. Bader, Worlds Apart in Chemistry: A Personal Tribute to J. C. Slater, *J. Phys. Chem. A*, 2011, **115**, 12667–12676.
4 G. B. Bacskay and S. Nordholm, Covalent Bonding: The Fundamental Role of the Kinetic Energy, *J. Phys. Chem. A*, 2013, **117**, 7946–7958.
5 M. W. Schmidt, J. Ivanic and K. Ruedenberg, Covalent Bonds are Created by the Drive of Electron Waves to Lower Their Kinetic Energy Through Expansion, *J. Chem. Phys.*, 2014, **140**, 204104.
6 P. Needham, The Source of Chemical Bonding, *Stud. Hist. Philoso. Sci.*, 2014, **45**, 1–13.
7 K. T. Tang and J. P. Toennies, An Improved Simple Model for the van der Waals Potential Based on Universal Damping Functions for the Dispersion Coefficients, *J. Chem. Phys.*, 1984, **80**, 3726–3741.
8 P. G. Hajigeorgiou and R. J. Le Roy, A "Modified Lennard-Jones Oscillator" Model for Diatom Potential Functions, *J. Chem. Phys.*, 2000, **112**, 3949–3957.
9 K. Cahill and V. A. Parsegian, Rydberg–London Potential for Diatomic Molecules and Unbonded Atom Pairs, *J. Chem. Phys.*, 2004, **121**, 10839–10842.
10 J. C. Xie, S. K. Mishra, T. Kar and R.-H. Xie, Generalized Interatomic Pair-Potential Function, *Chem. Phys. Lett.*, 2014, **605–606**, 137–146.
11 B. Ibarra-Tandi, A. Lira and J. López-Lemus, Effect of Softness on Relative Adsorption for Binary Mixtures of Simple Fluids, *J. Mol. Liq.*, 2013, **185**, 62–69.
12 R.-H. Xie and P. S. Hsu, Universal Reduced Potential Function for Diatomic Systems, *Phys. Rev. Lett.*, 2006, **96**, 243201.
13 J. Tellinghuisen, S. D. Henderson, D. Austin, K. P. Lawley and R. J. Donovan, Reduced Potential-Energy Curves for Diatomic Molecules, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1989, **39**, 925–930.
14 T.-C. Lim, Relationship and Discrepancies Among Typical Interaction Potential Functions, *Chin. Phys. Lett.*, 2004, **21**, 2167–2170.
15 T.-C. Lim, Connection Among Classical Interatomic Potential Functions, *J. Math. Chem.*, 2004, **36**, 261–269.
16 P. M. Morse, Diatomic Molecules According to the Wave Mechanics. II. Vibrational Levels, *Phys. Rev.*, 1929, **34**, 57–64.
17 S. S. Xantheas and J. C. Werhahn, Universal Scaling of Potential Energy Functions Describing Intermolecular Interactions. I. Foundations and Scalable Forms of New Generalized Mie, Lennard-Jones, Morse, and Buckingham Exponential-6 Potentials, *J. Chem. Phys.*, 2014, **141**, 064117.
18 A. C. Legon, A reduced radial potential energy function for the halogen bond and the hydrogen bond in complexes B-XY and B-HX, where X and Y are halogen atoms, *Phys. Chem. Chem. Phys.*, 2014, **16**, 12415.
19 J. E. Jones, On the Determination of Molecular Fields. II. From the Equation of State of a Gas, *Proc. R. Soc. London, Ser. A*, 1924, **106**, 463–477.
20 P. G. Hajigeorgiou, An Extended Lennard-Jones Potential Energy Function for Diatomic Molecules: Application to Ground Electronic States, *J. Mol. Spectrosc.*, 2010, **263**, 101–110.
21 G. Mie, Zur Kinetischen Theorie der Einatomigen Körper, *Ann. Phys.*, 1903, **316**, 657–697.
22 R. Rydberg, Graphische Darstellung Einiger Bandenspektroskopischer Ergebnisse, *Z. Phys.*, 1932, **73**, 376–385.
23 O. Klein, Zur Berechnung von Potentialkurven für Zweiatomige Moleküle mit Hilfe von Spektraltermen, *Z. Phys.*, 1932, **76**, 226–235.
24 A. L. G. Rees, The Calculation of Potential-Energy Curves from Band-Spectroscopic Data, *Proc. Phys. Soc., London*, 1947, **59**, 998–1008.
25 R. J. Le Roy, University of Waterloo Chemical Physics Research Report, CP-657R, 2004.

26 F. Jenč and B. A. Brandt, Reduced ab Initio Theoretical Internuclear Potentials of Diatomic Molecules, *Theor. Chim. Acta*, 1987, **72**, 411–432.

27 D. J. Nesbitt and M. S. Child, Rotational-RKR Inversion of Intermolecular Stretching Potentials: Extension to Linear Hydrogen Bonded Complexes, *J. Chem. Phys.*, 1993, **98**, 478–486.

28 R. R. Lucchese, C. K. Rosales, L. A. Rivera-Rivera, B. A. McElmurry, J. W. Bevan and J. R. Walton, A Unified Perspective on the Nature of Bonding in Pairwise Interatomic Interactions, *J. Phys. Chem. A*, 2014, **118**, 6287–6298. In this reference, the notation $V(R)$ corresponds to the notation $E(R)$ used in the current work.

29 J. R. Walton, L. A. Rivera-Rivera, R. R. Lucchese and J. W. Bevan, Morse, Lennard-Jones, and Kratzer potentials: A canonical perspective with applications, *J. Phys. Chem. A*, 2016, **120**, 8347–8359.

30 J. R. Walton, L. A. Rivera-Rivera, R. R. Lucchese and J. W. Bevan, A General Transformation to Canonical Form for Potentials in Pairwise Interatomic Interactions, *Phys. Chem. Chem. Phys.*, 2015, **17**, 14805–14810.

31 J. R. Walton, L. A. Rivera-Rivera, R. R. Lucchese and J. W. Bevan, Canonical Potentials and Spectra within the Born-Oppenheimer Approximation, *J. Phys. Chem. A*, 2015, **119**, 6753–6758. In this reference, the notation $V(R)$ corresponds to the notation $E(R)$ used in the current work.

32 J. R. Walton, L. A. Rivera-Rivera, R. R. Lucchese and J. W. Bevan, From H_2^+ to the Multidimensional Potential of the Intermolecular Interaction Ar·HBr: A Canonical Approach, *Chem. Phys. Lett.*, 2015, **639**, 63–66.

33 J. R. Walton, L. A. Rivera-Rivera, R. R. Lucchese and J. W. Bevan, A Canonical Approach to Multi-Dimensional van der Waals, Hydrogen-Bonded, and Halogen-Bonded Potentials, *Chem. Phys.*, 2016, **469–470**, 60–64.

34 J. R. Walton, L. A. Rivera-Rivera, R. R. Lucchese and J. W. Bevan, Canonical Approaches to Applications of the Virial Theorem, *J. Phys. Chem. A*, 2016, **120**, 817–823.

35 J. R. Walton, L. A. Rivera-Rivera, R. R. Lucchese and J. W. Bevan, A Canonical Approach to Forces in Molecules, *Chem. Phys.*, 2016, **474**, 52–58.

36 J. R. Walton, L. A. Rivera-Rivera, R. R. Lucchese and J. W. Bevan, Canonical Force Distributions in Pairwise Interatomic Interactions from the Perspective of the Hellmann-Feynman Theorem, *J. Phys. Chem. A*, 2016, **120**, 3718–3725.

37 R. P. Feynman, Forces in Molecules, *Phys. Rev.*, 1939, **56**, 340–343.

38 H. Hellmann, *Einführung in die Quantenchemie*, Franz Deuticke, Leipzig and Vienna, 1937, p. 285.

39 M. Born and R. Oppenheimer, Zur Quantentheorie der Molekeln, *Ann. Phys.*, 1927, **389**, 457–484.