Lawrence Berkeley National Laboratory

Title
From H2+ to the multidimensional potential of the intermolecular interaction Ar·HBr: A canonical approach

Permalink
https://escholarship.org/uc/item/2nn4p4c9

Authors
Walton, Jay R
Rivera-Rivera, Luis A
Lucchese, Robert R
et al.

Peer reviewed

From H_2^+ to the Multidimensional Potential of the Intermolecular Interaction Ar·HBr: A Canonical Approach

Jay R. Walton

Department of Mathematics, Texas A&M University, College Station, Texas 77843-3368

Luis A. Rivera-Rivera, Robert R. Lucchese, and John W. Bevan[*]

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

Abstract

A new approach to the accurate generation of multidimensional intermolecular interaction potentials is demonstrated. The basis for evaluating this application is the available very accurate 3-dimensional morphed potential of Ar•HBr. Starting from the well-defined potential of the simplest molecule, the diatomic H_2^+, a recently developed canonical approach is applied and used with sufficient additional polyatomic data to generate the adiabatic intermolecular interaction potential in Ar•HBr, with HBr in the vibrational ground state. This represents the first application of canonical transformations to a higher vibrationally dimensional molecular system, in this case, Ar•HBr. Results indicate intrinsic bonding characteristics inherent to both systems.

---

[*] To whom correspondence should be addressed. E-mail: bevan@mail.chem.tamu.edu

1. Introduction

The concept of the potential energy surface has been and continues to be pivotal in understanding, characterizing, and predicting properties associated with molecules and interactions between molecules [1-9]. Much effort has been made to develop formulations which can directly describe the interaction between two atoms in a molecule or atomic dimer as well as form the basis to model the interaction between larger molecular systems [10-19]. An extensive number of empirical, theoretical, and semi-empirical approaches to the determination potential energy surfaces of intermolecular interactions now exist.

Recently, we introduced formulations for accurately generating equilibrium dissociation energies D_e as well as explicit force-based transformations [20] to a canonical potential for both diatomic and two body intermolecular interactions [21]. The term canonical potential for a class of molecules refers 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. Different classes of representative ground electronic state pairwise interatomic interactions were 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 1-dimensional dissociative coordinates in intermolecular Ar-HBr, OC-HF, and OC-Cl_2 were investigated throughout their ground state bound potentials.

Even more recently, we generalized formulation of canonical transformations [21] and spectra, and used them to investigate the concept of a canonical potential strictly within the Born-Oppenheimer approximation [22]. Specifically, from the single canonical potential of the simplest molecule, H_2^+, we generated the potentials of a set of different molecules explicitly. This set was chosen to include the most accurately available ground electronic state pairwise interaction potentials in H_2, HD, D_2, HeH^+, and LiH. The efficacy of the canonical approach was then stringently tested by direct comparison of the predicted eigenvalues of all vibrational states in the ground electronic state bound potentials of the molecular systems considered with those of the corresponding most accurately known Born-Oppenheimer eigenvalues currently available. Such deviations were demonstrated to be less than 2 cm^{-1} for all vibrational states in H_2, HD, D_2, HeH^+, and LiH with an average standard deviation of 0.27 cm^{-1} for the 87 states considered [22].

The question now arises whether this canonical approach can be developed to generate the multidimensional potential energy surfaces of polyatomic systems. In this case, we will investigate this possibility in the intermolecular interaction Ar•HBr. The high resolution microwave spectrum [23] of Ar•HBr was first investigated, but subsequent submillimeter and infrared investigations [24, 25] lead to accurate determination of D_0 [26] and increasingly accurate morphed 3-dimensional potentials [27-29]. This extremely accurate potential now provides the accurate data necessary for proposed investigations.

2. Method

For the present study, the reference potential is selected to be that for H_2^+, the

simplest molecule. Considering the potential $E(R)$ with associated force distribution

$F(R) = -E'(R)$, we define R_e and R_m to be the equilibrium nuclear separation, that is,

the internuclear distance for which $F(R_e) = 0$, and the nuclear separation distance of

maximum attractive force, that is $F(R_m) = F_m = \max_{R > R_e} F(R)$, respectively. We note that

$R_e < R_m$. Dimensionless, canonical potentials are constructed for both the "attractive" and

"repulsive" sides of a potential as follows.

a. Attractive Side

The dimensionless canonical potential $\tilde{V}_{ej}^a(x; \gamma)$ for $0 \le x \le 1$ and $j = 0, 1, \ldots$ is

defined by:

$$\tilde{V}_{ej}^a(x; \gamma) = \frac{V\left(x\gamma R_j^a + (1 - x\gamma)R_e\right) - V\left(R_e\right)}{V\left(\gamma R_j^a + (1 - \gamma)R_e\right) - V\left(R_e\right)}.$$ (1)

Similarly, the potential $\tilde{V}_{ij}^a(x; \gamma)$ for $0 \le x \le 1$ and $0 \le i < j$ is defined by:

$$\tilde{V}_{ij}^a(x; \gamma) = \frac{V\left(x\gamma R_j^a + (1 - x\gamma)R_i^a\right) - V\left(R_i^a\right)}{V\left(\gamma R_j^a + (1 - \gamma)R_i^a\right) - V\left(R_i^a\right)}.$$ (2)

In Eqs. (1) and (2), R_j^a is defined by: $F\left(R_j^a\right) = F_m / 2^j$. The transformations to the

canonical forms in Eqs. (1) and (2) are readily inverted giving Eq. (1) with

$x = (R - R_e) / (\gamma(R_j^a - R_e))$:

$$V(R) = V\left(R_e\right) + V\left(\gamma R_j^a + (1 - \gamma)R_e\right)\tilde{V}_{ej}^a(x; \gamma), \quad \text{for} \quad R_e < R < \left(\gamma R_j^a + (1 - \gamma)R_e\right)$$ (3)

and for Eq. (2) $x = (R - R_i^a) / (\gamma(R_j^a - R_i^a))$:

$$V(R) = V\left(R_i^a\right) + V\left(\gamma R_j^a + (1 - \gamma)R_i^a\right)\tilde{V}_{ij}^a(x; \gamma), \quad \text{for} \quad R_i^a < R < \left(\gamma R_j^a + (1 - \gamma)R_i^a\right)$$ (4)

b. Repulsive Side

The dimensionless canonical potential $\tilde{V}^{\mathrm{r}}_{ej}(x;\gamma)$ for $0 \le x \le 1$ and $j = 0, 1, \ldots$ is

defined by:

$$\tilde{V}^{\mathrm{r}}_{ej}(x;\gamma) = \frac{V\left(x\gamma R^{\mathrm{r}}_{j} + (1-x\gamma)R_{\mathrm{e}}\right) - V\left(R_{\mathrm{e}}\right)}{V\left(\gamma R^{\mathrm{r}}_{j} + (1-\gamma)R_{\mathrm{e}}\right) - V\left(R_{\mathrm{e}}\right)}. \tag{5}$$

Similarly, the potential $\tilde{V}^{\mathrm{r}}_{ij}(x;\gamma)$ for $0 \le x \le 1$ and $0 \le i < j$ is defined by:

$$\tilde{V}^{\mathrm{r}}_{ij}(x;\gamma) = \frac{V\left(x\gamma R^{\mathrm{r}}_{j} + (1-x\gamma)R^{\mathrm{r}}_{i}\right) - V\left(R^{\mathrm{r}}_{i}\right)}{V\left(\gamma R^{\mathrm{r}}_{j} + (1-\gamma)R^{\mathrm{r}}_{i}\right) - V\left(R^{\mathrm{r}}_{i}\right)}. \tag{6}$$

In Eqs. (5) and (6) R^{r}_{j} is defined by: $F\left(R^{\mathrm{r}}_{j}\right) = F_{\mathrm{m}} 2^{j}$. The transformations to the canonical

forms in Eqs. (5) and (6) are readily inverted giving Eq. (5) with

$x = (R - R_{\mathrm{e}})/(\gamma(R^{\mathrm{r}}_{j} - R_{\mathrm{e}}))$:

$$V(R) = V\left(R_{\mathrm{e}}\right) + V\left(\gamma R^{\mathrm{r}}_{j} + (1-\gamma)R_{\mathrm{e}}\right)\tilde{V}^{\mathrm{r}}_{ej}(x;\gamma), \quad \text{for} \quad \left(\gamma R^{\mathrm{r}}_{j} + (1-\gamma)R_{\mathrm{e}}\right) < R < R_{\mathrm{e}} \tag{7}$$

and Eq. (6) with $x = (R - R^{\mathrm{r}}_{i})/(\gamma(R^{\mathrm{r}}_{j} - R^{\mathrm{r}}_{i}))$:

$$V(R) = V\left(R^{\mathrm{r}}_{i}\right) + V\left(\gamma R^{\mathrm{r}}_{j} + (1-\gamma)R^{\mathrm{r}}_{i}\right)\tilde{V}^{\mathrm{r}}_{ij}(x;\gamma), \quad \text{for} \quad \left(\gamma R^{\mathrm{r}}_{j} + (1-\gamma)R^{\mathrm{r}}_{i}\right) < R < R^{\mathrm{r}}_{i} \tag{8}$$

Complete details of the canonical transformations can be found in Ref. [22].

3. Results and Discussion

Figure 1 shows different radial cuts at 10° intervals through the adiabatic potential

of Ar•HBr, with HBr in the vibrational ground state, associated with different angles

θ which corresponds to linear isomer Ar-HBr ($\theta = 0°$) and linear isomer Ar-BrH

($\theta = 180°$). The shapes of these curves together with the results presented in Ref. 22

indicate that the adiabatic potential of Ar•HBr is canonical. Figure 2, shows the corresponding results for $\theta = 10°$, 90°, and 170° which are selected for subsequent special consideration with respect to Figs. 3a and 3b. Figure 3a demonstrates the canonical nature of the radial potential of Ar•HBr at the specifically chosen angles of $\theta = 10°$, 90°, and 170° as they are transformed to the same canonical curve. Clearly, corresponding plots exist for all angles from $\theta = 0°$ to 180° covering the whole angular potential for the adiabatic potential of Ar•HBr, confirming the canonical characteristics of the intermolecular potential. The canonical radial potential of Ar•HBr at $\theta = 10°$, 90°, and 170°, which have been represented in Fig. 3a has now been extended to include the corresponding H_2^+ canonical potential, as shown in Fig. 3b. This demonstrates that to high accuracy, the potentials of both Ar•HBr and H_2^+ are canonical and furthermore suggests that the radial canonical potential of the simplest molecule H_2^+ [30] can be used to generate the multidimensional potential of Ar•HBr provided there is sufficient independent data available for that potential from another independent source.

The multidimensional adiabatic potential of Ar•HBr can be approximated by extending the 1-dimensional radial procedure introduced in Ref. [22] (Eqs. 10-15). Specifically, one takes a sequence of angles $\theta_1,...,\theta_n$, and applies the Eqs. 10-15 of Ref. [22] to represent each of the radial potentials $E(\theta_k,R)$ using a selection of dyadic radial values $R_j^a(\theta_k)$. One then uses piecewise affine transformations applied to portions of the canonical radial potential (H_2^+) onto corresponding portions of the 1-dimensional radial potentials $E(\theta_k,R)$ for each angle θ_k as illustrated on Fig. 1 in Ref. [22]. For illustrative purposes in this work, for each θ_k, eight R-values { $R_j^a(\theta_k) : j=1,2,3,4$} along with $R_e(\theta_k)$

are used in the construction. As shown in Ref. [22], more accurate representations can be obtained by using more R-values. Spline interpolation is then used to approximate $E(\theta,R)$ for all other angular values θ.

In Fig. 4, we present the generated adiabatic potential of Ar•HBr, with HBr in the vibrational ground state, generated by using the H_2^+ canonical potential as a reference molecule over the range -200 to +200 cm^{-1} while the radial coordinate covers the range 2.50 to 6.60 Å. The relative error in the surface is given in Fig. 5, and is approximately less than the very small value of 0.08% over the whole surface, which gives considerable confidence in the accuracy of this canonical approach in this particular case. Since the adiabatic potential has been used to investigate the rovibrational dynamics of Ar•HBr, we have chosen to use the adiabatic potential in this work and not the full 3-dimensional potential. The 3-dimensional potential can be approximated following the above procedure for different values of the HBr bond length. In the adiabatic potential, it is pertinent to note the HBr bond length is vibrationally averaged as a function of R and θ. In addition, this canonical transformation is only completely applicable where there is an attractive force in the radial direction, which occurs in all the systems we have considered.

The different classes of representative ground electronic state pairwise interatomic interactions that we referenced to a chosen canonical potential can now be discussed in the context of the current result [20,21]. Specifically, the accurately determined potentials of the diatomic molecules H_2, H_2^+, HF, LiH, argon dimer, and 1-dimensional dissociative coordinates in intermolecular Ar-HBr, OC-HF, and OC-Cl$_2$ were shown to be canonical. The H_2^+ was a member of this series which implies that the other

members of this series command similar canonical behavior with respect to the potential of Ar•HBr currently under consideration.

4. Conclusions

From a consideration of the adiabatic potential energy surface of Ar•HBr, with HBr in the vibrational ground state, we demonstrate that the canonical transformation with respect to the radial degree of freedom is independent of the angular degree of freedom of the potential energy surface. Furthermore, we have demonstrated that this multidimensional potential can be correlated with the corresponding canonical potential of the simplest molecule, the one electron diatomic H_2^+. Consequently, the potential energy surface of this intermolecular interaction can be accurately generated from the canonical ground state potential of H_2^+ together with sufficient independent additional data relevant to the polyatomic such as that supplied by experiment or reliable quantum mechanical calculation. This indicates that the canonical approach has widespread potential applications in characterization of potential energy surfaces of molecular systems with vibrationally higher dimensions both in intramolecular and intermolecular systems. Hence, this approach provides a unified perspective on chemical bonding in polyatomic systems that should be the subject of intense further study.

8

and the Institute for Applied Mathematics and Computational Science at Texas A&M University.

References

1. I. G. Kaplan, Intermolecular Interactions: Physical Picture, Computational Methods and Model Potentials, Wiley, 2006.

2. A. J. Stone, The Theory of Intermolecular Forces, 2nd Edition, Clarendon Press, 2013.

3. P. Jensen and P. Bunker, Computational Molecular Spectroscopy, Wiley, 2000.

4. I. M. Torrens, Interatomic Potentials, Academic Press, 1972, p 3.

5. H. M. Hulburt and J. O. Hirschfelder, J. Chem. Phys. 9, 61 (1941).

6. A. D. Buckingham, Phil. Trans. R. Soc. Lond. B 272, 5 (1975).

7. J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, Molecular Theory of Gases and Liquids, Wiley, 1954.

8. J. H. Harding, Interatomic Potentials: A user guide, in Computer simulation in Materials Science edited by M. Meyer and V. Pontikis (Kluwer Academic Publishers: Dordrecht, 1991)

9. S. B. Sinnott and D. W. Brenner, MRS Bulletin 37, 469 (2012).

10. C. Leforestier, L. B. Braly, K. Lui, M. J. Elrod, and R. J. Saykally, J. Chem. Phys. 106, 8527 (1997).

11. Y. Qiu and Z. Bacic, J. Chem. Phys. 106, 2158 (1997).

12. G. Brocks, A. van der Avoird, B. T. Sutcliffe, and J. Tennyson, Mol. Phys. 50, 1025 (1983).

13. A. van der Avoird, P. E. S. Wormer, and R. Moszynski, in *Molecular Interactions from van der Waals to Strongly Bound Complexes*, edited by S. Scheiner (John Wiley & Sons, Chichester, 1997), p. 105.

14. V. Babin, C. Leforestier, and F. I. Paesani, J. Chem. Theory Comput. 9, 5395 (2013).

15. P.E.S. Wormer and Ad van der Avoird, Chem. Rev. 100, 4109 (2000).

16. G. Chałasinski and M. M. Szczesniak, Chem. Rev. 100, 4227 (2000).

17. A. K. Samanta, G. Czakó, Y. Wang, J. S. Mancini, J. M. Bowman, and H. Reisler, Acc. Chem. Res. 47, 2700, (2014).

18. S. R. Gadre, S. D. Yeole, and N. Sahu, Chem. Rev. 114, 12132 (2014).

19. L. A. Rivera-Rivera, Z. Wang, B. A. McElmurry, R. R. Lucchese, J. W. Bevan, and G. Kanschat, Chem. Phys. 390, 42 (2011).

20. R. R. Lucchese, C. K. Rosales, L. A. Rivera-Rivera, B. A. McElmurry, J. W. Bevan, and J. R. Walton, J. Phys. Chem. A 118, 6287 (2014).

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

22. J. R. Walton, L. A. Rivera-Rivera, R. R. Lucchese, and J. W. Bevan, J. Phys. Chem. A 119, 6753 (2015).

23. M. R. Keenan, E. J. Campbell, T. J. Balle, L. W. Buxton, T. K. Minton, P. D. Soper, and W. H. Flygare, J. Chem. Phys. 72, 3070 (1980).

24. J. Han, A. L. McIntosh, C. L. Hartz, R. R. Luchese, and J. W. Bevan, Chem. Phys. Lett. 265, 209 (1997).

25. B. A. McElmurry, R. R. Lucchese, J. W. Bevan, I. I. Leonov, S. P. Belov, and A. C. Legon, J. Chem. Phys. 119, 10687 (2003).

26. Z. Wang, A. L. McIntosh, B. A. McElmurry, J. Walton, R. R. Lucchese, and J. W. Bevan, J. Phys. Chem. A 109, 8168 (2005).

27. J. Castillo-Chara, R. R. Lucchese, and J. W. Bevan, J. Chem. Phys. 115, 899 (2001).

28. S. P. Belov, B. A. McElmurry, R. R. Lucchese, J. W. Bevan, and I. Leonov, Chem. Phys. Lett. 370, 528 (2003).

29. F. F. Willaert, B. A. McElmurry, R. R. Lucchese, and J. W. Bevan, Chem. Phys. Lett. 460, 325 (2008).
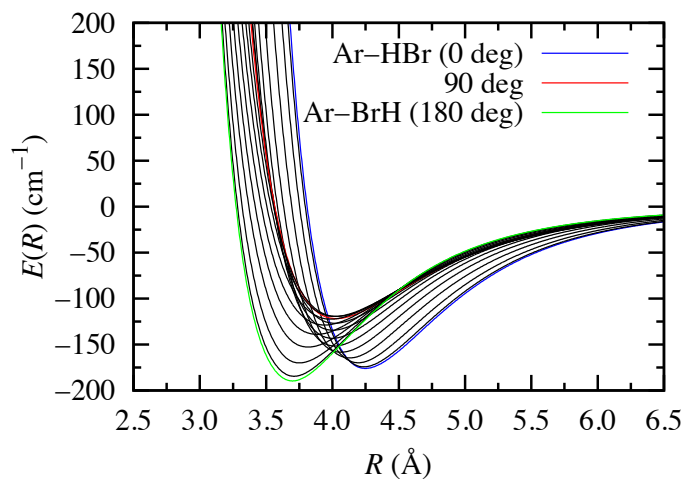
30. Private communication, D. W. Schwenke supplied the H_2^+ data.

Figure 1. Radial cuts of the adiabatic potential of Ar•HBr, with HBr in the vibrational ground state, at different values of θ from 0° to 180° every 10°.
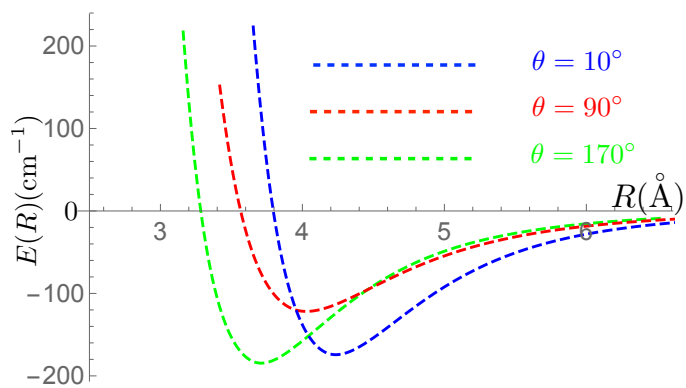
Figure 2. Radial cuts of the adiabatic potential of Ar•HBr, with HBr in the vibrational ground state, at $\theta = 10°$, 90°, and 170°.
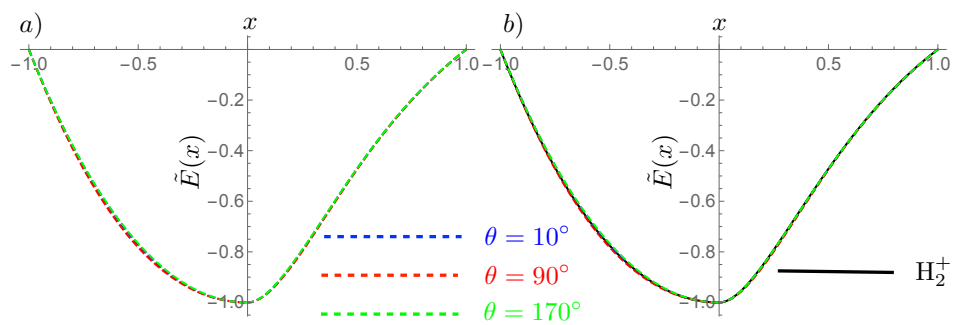
Friday, June 26, 15

Figure 3a. Canonical radial potential of Ar•HBr at $\theta = 10°$, 90°, and 170°. Figure 3b. Canonical radial potential of Ar•HBr at $\theta = 10°$, 90°, and 170°, with the addition of the H_2^+ canonical potential.
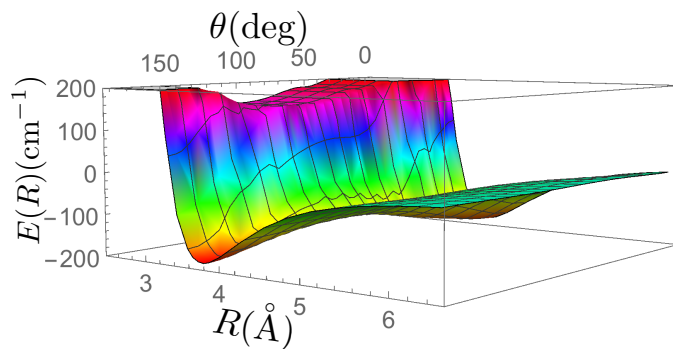
Figure 4. Generated adiabatic potential energy surface of Ar•HBr, with HBr in the vibrational ground state, constructed from the 1-dimensional potential curve for H_2^+.
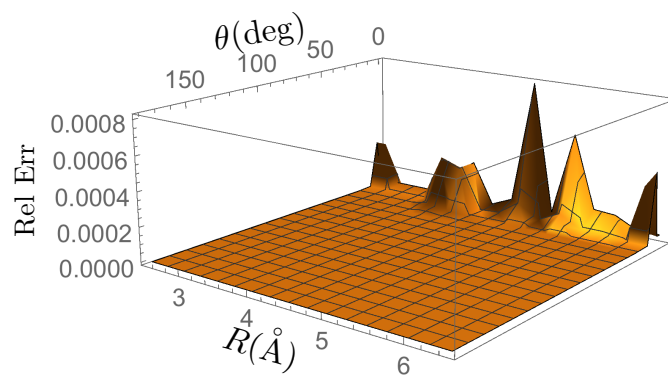
Figure 5. Pointwise relative error on the estimated adiabatic potential energy surface of Ar•HBr shown in Figure 4, with HBr in the vibrational ground state, compared to the morphed potential of Ar•HBr.