A CANONICAL APPROACH TO MULTI-DIMENSIONAL VAN DER WAALS, HYDROGEN-BONDED, AND HALOGEN-BONDED POTENTIALS

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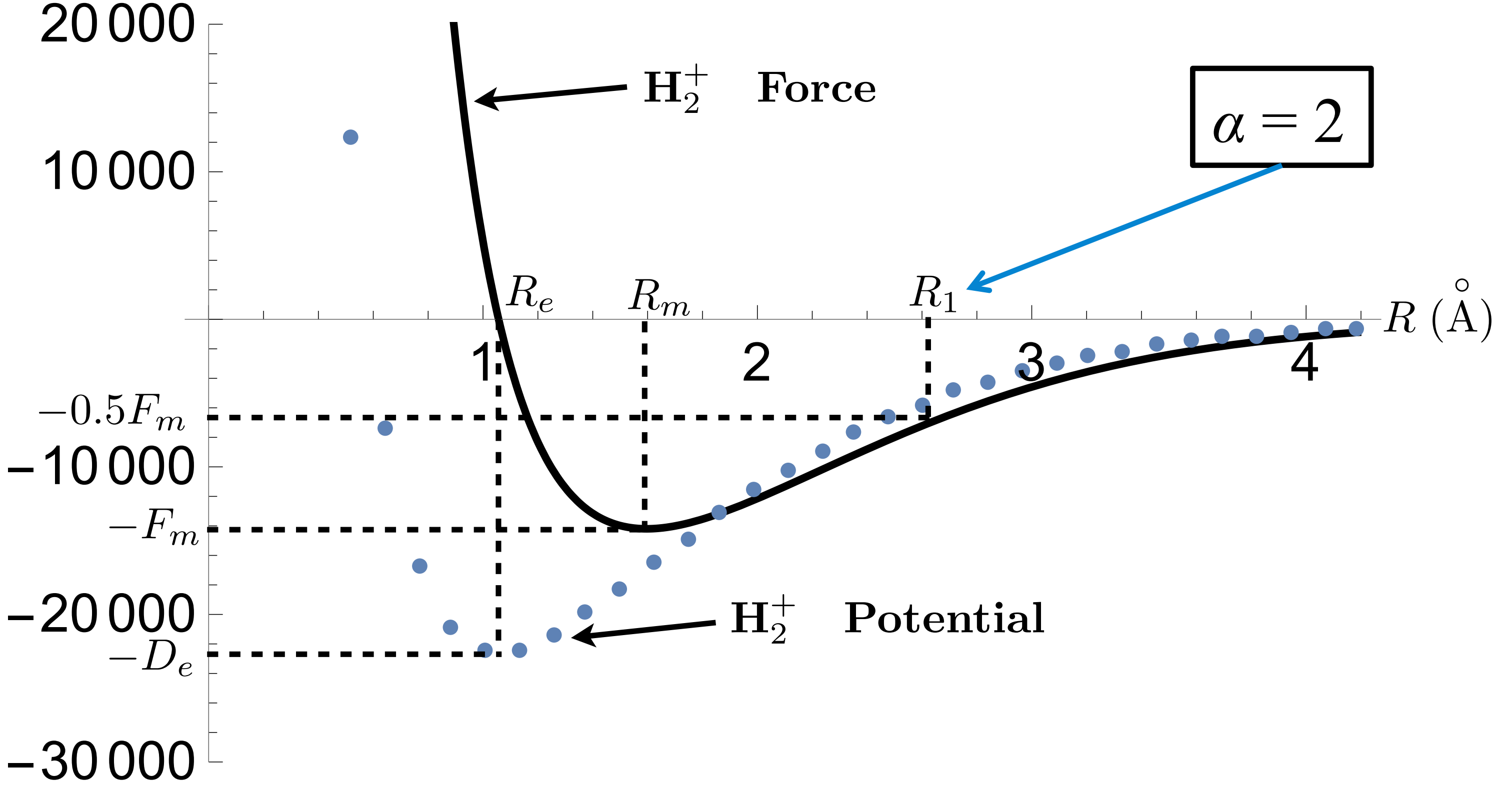
Outline

- Canonical Potentials in Multidimensional Systems
- The Virial Theorem
- The Origin of the Canonical Transformations

Feynman Force for H_2^+ Molecule



$$F(R_{rj}) = F_m \alpha^j \qquad F(R_{aj}) = -F_m / \alpha^j$$

Canonical Transformations
Potential

$$\tilde{E}(x;R_j,R_{j+1}) := \frac{E(R_j + x(R_{j+1} - R_j)) - E(R_j)}{E(R_{j+1}) - E(R_j)} \quad \text{for} \quad 0 \le x \le 1$$

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

$$\tilde{E}_1 \approx \tilde{E}_2 \quad \text{for } 0 \le x \le 1$$

Canonical Transformations
Force

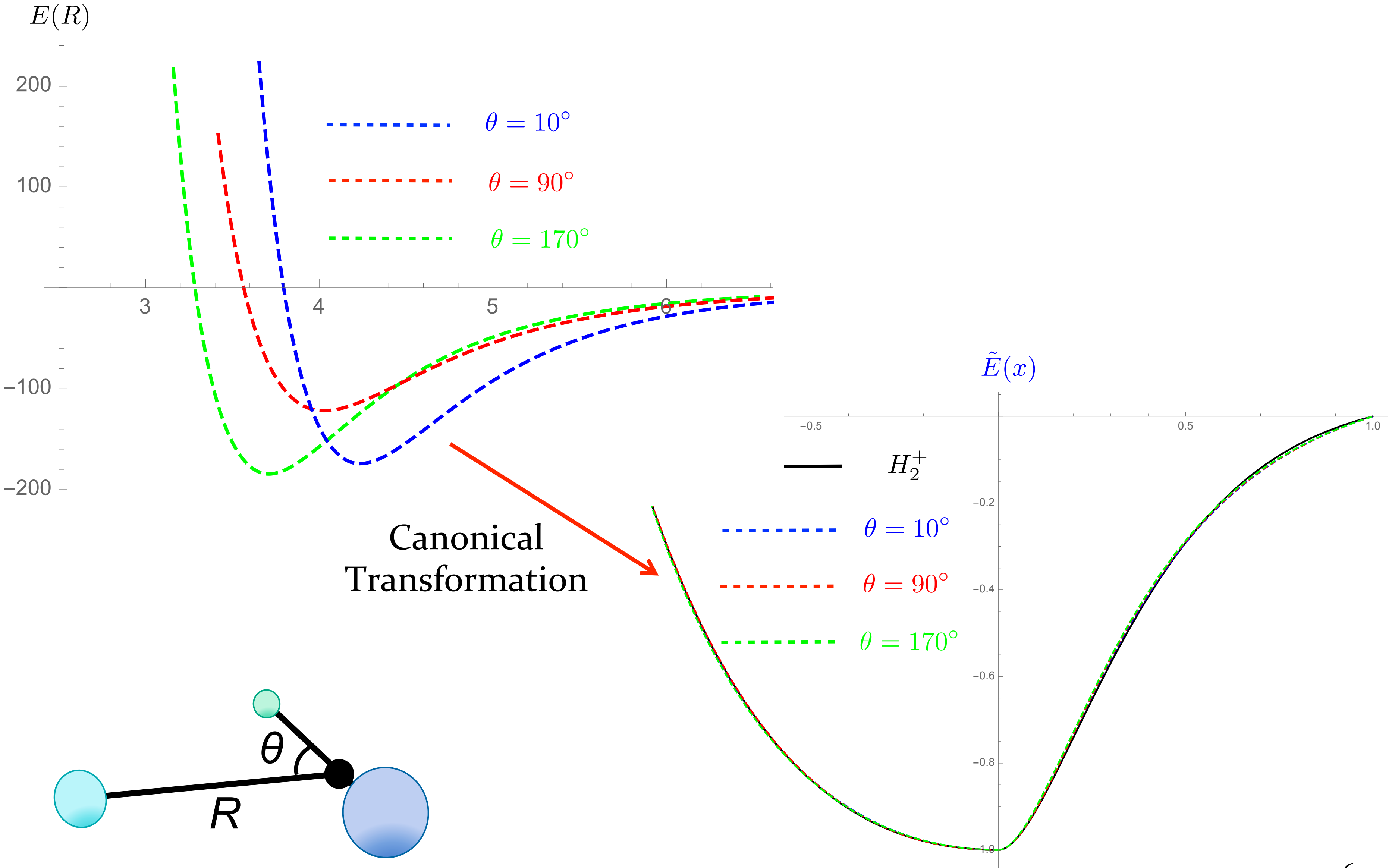
$$\tilde{F}(x;R_j,R_{j+1}) = \frac{F(R_j + x(R_{j+1} - R_j)) - F(R_j)}{F(R_{j+1}) - F(R_j)} \quad \text{for} \quad 0 \le x \le 1$$

$$F_1(R) = F_1(R_j) + \Big(F_1(R_{j+1}) - F_1(R_j)\Big)\tilde{F}_1\left(\frac{R - R_j}{R_{j+1} - R_j}\right)$$

$$\approx F_1(R_j) + \Big(F_1(R_{j+1}) - F_1(R_j)\Big)\tilde{F}_2\left(\frac{R - R_j}{R_{j+1} - R_j}\right)$$

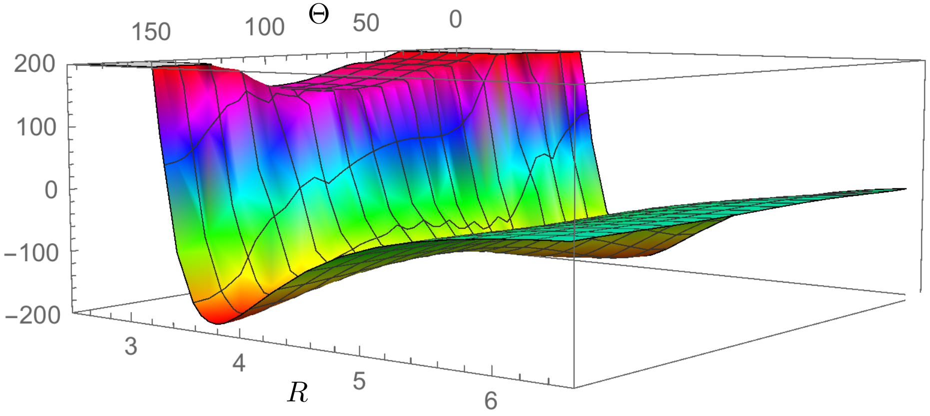
$$\tilde{F}_1 \approx \tilde{F}_2 \quad \text{for } 0 \le x \le 1$$

Multidimensional Systems: Ar-HBr

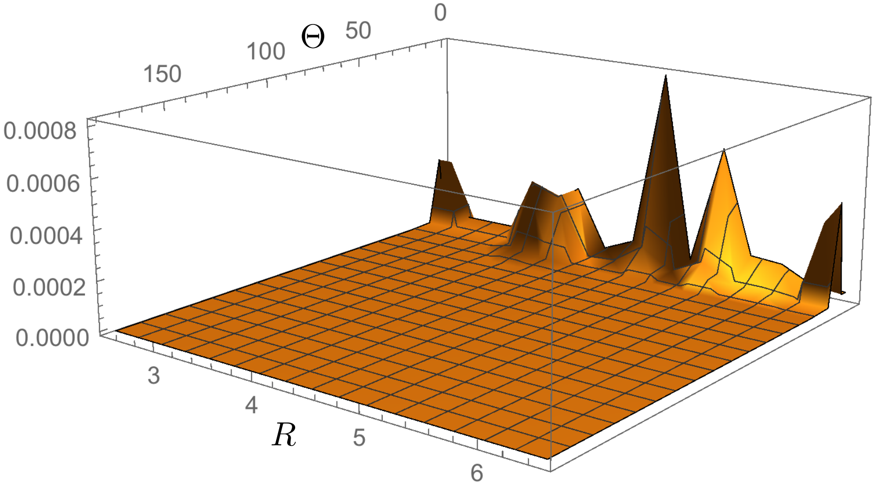


Canonical Transformation

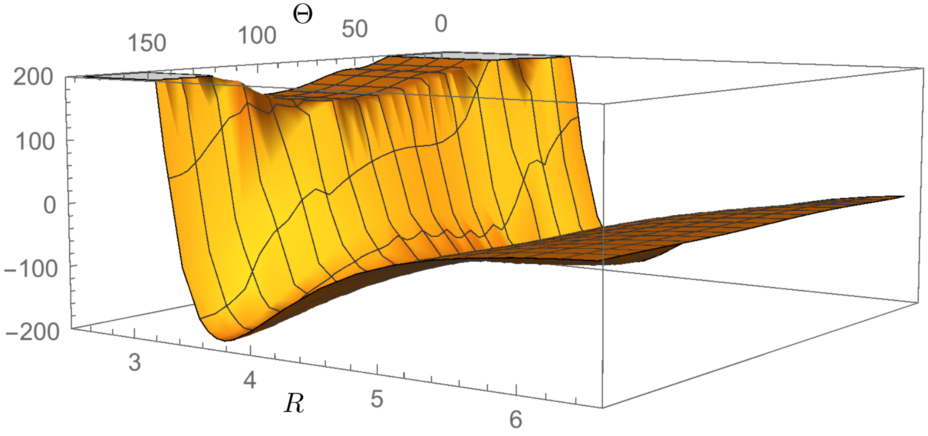
Ar-HBr 2-D Potential Surface: Canonical Approximation



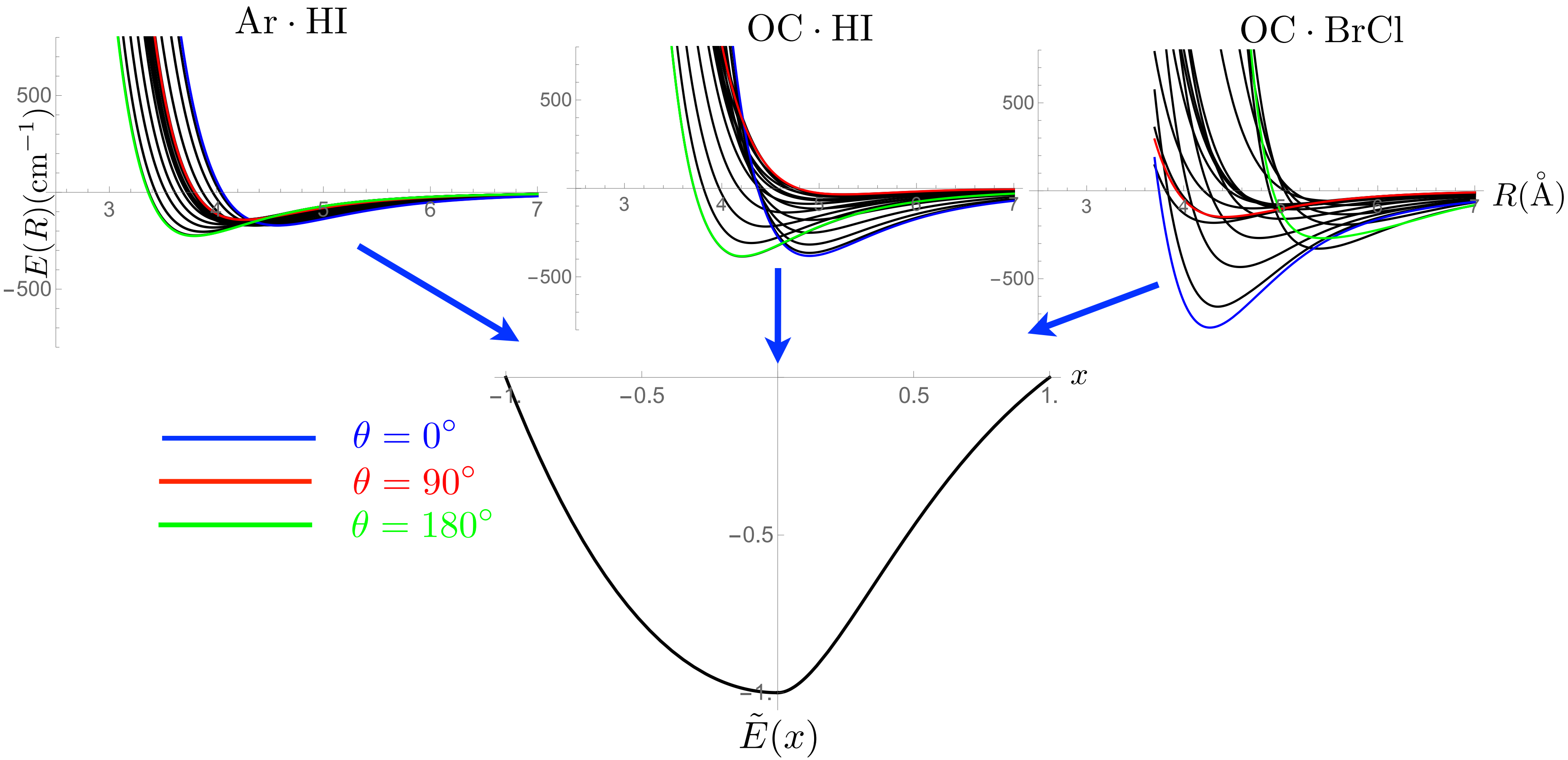
Relative Errors

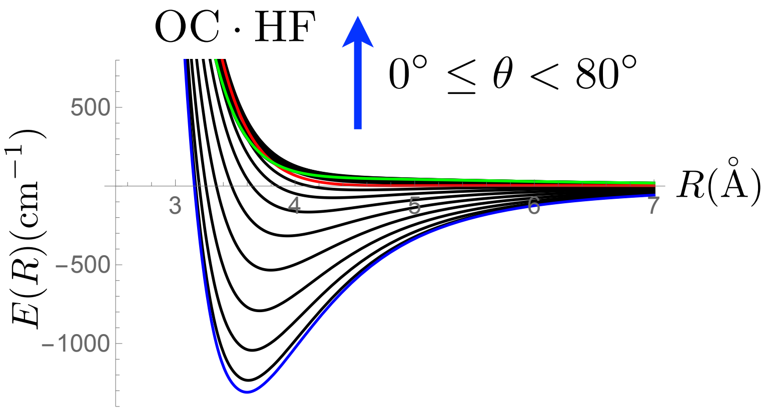


Ar-HBr 2-D Potential Surface: True

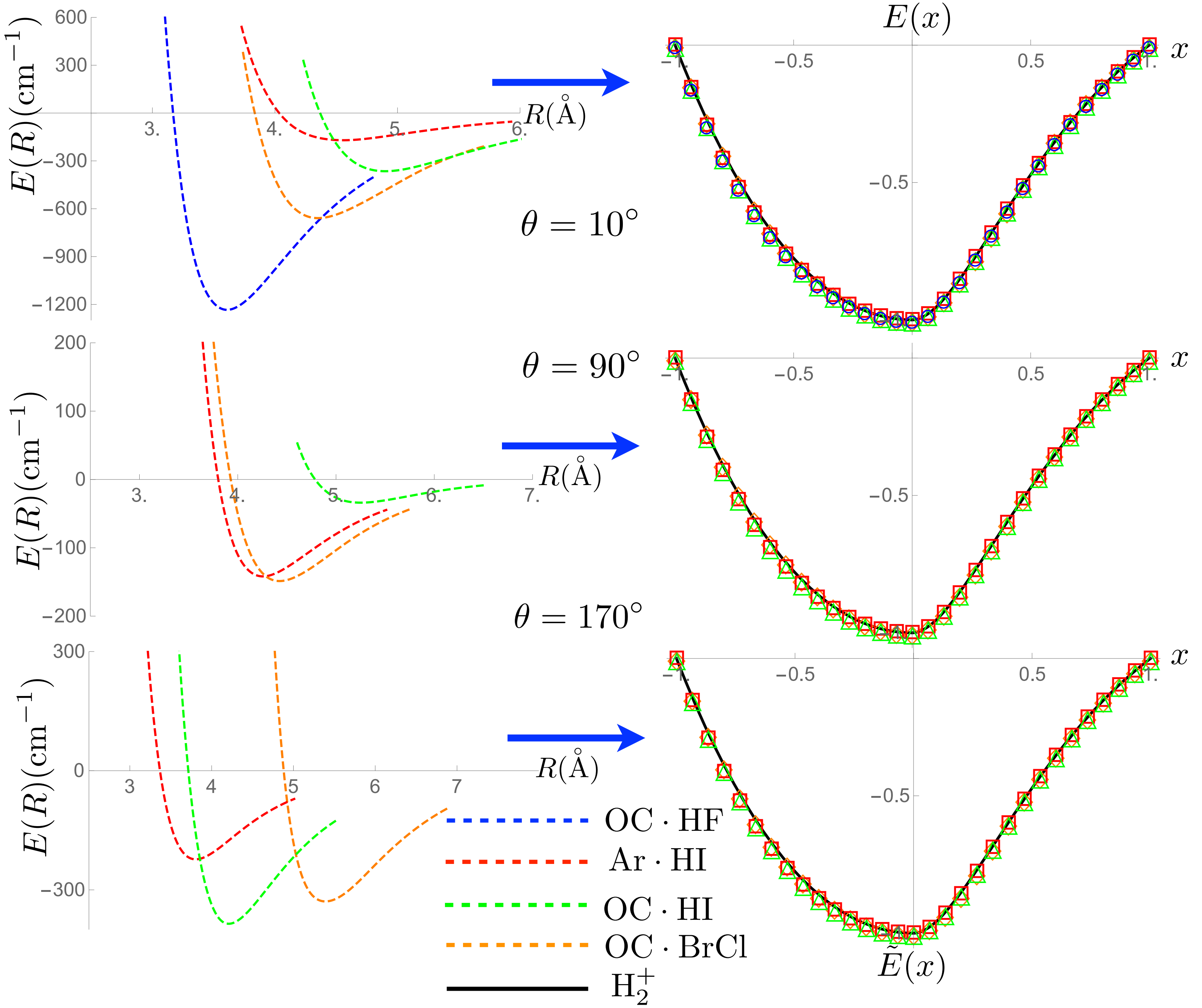


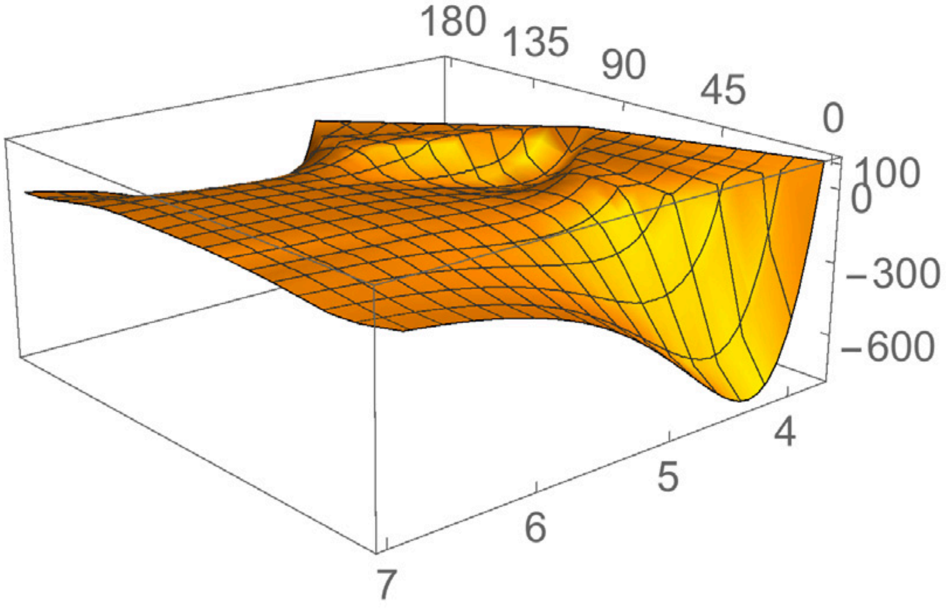
Walton et al. Chem. Phys. Lett. 639 (2015) 63.



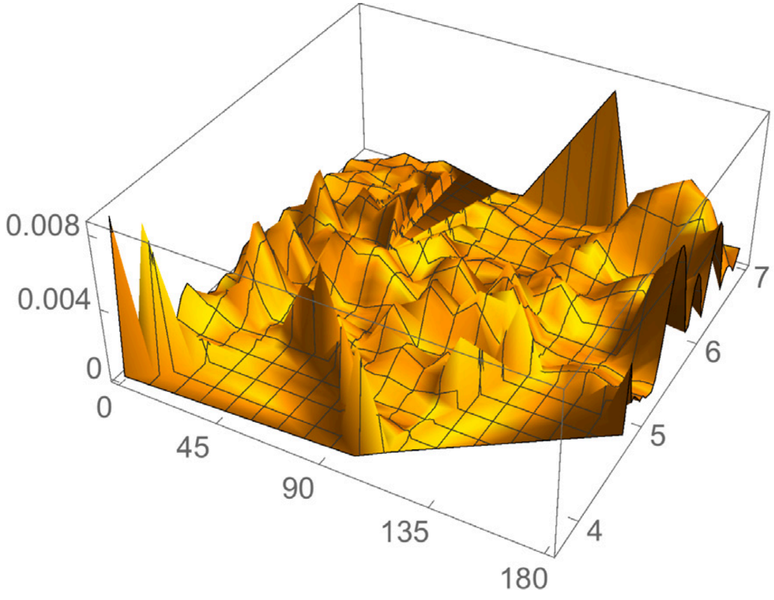


Walton et al.
Chem. Phys. 469-470
(2016) 60.


$E(R)(\mathrm{cm}^{-1})$
600
300
−300
−600
−900
−1200
3.
4.
5.
6.
$R(\text{Å})$
$\theta = 10^\circ$
$\tilde{E}(x)$
x
−1.
−0.5
0.5
1.
200
100
0
−100
−200
7.
$\theta = 90^\circ$
$\theta = 170^\circ$
−300
3
4
5
6
7
$\mathrm{OC}\cdot\mathrm{HF}$
$\mathrm{Ar}\cdot\mathrm{HI}$
$\mathrm{OC}\cdot\mathrm{HI}$
$\mathrm{OC}\cdot\mathrm{BrCl}$
H_2^+



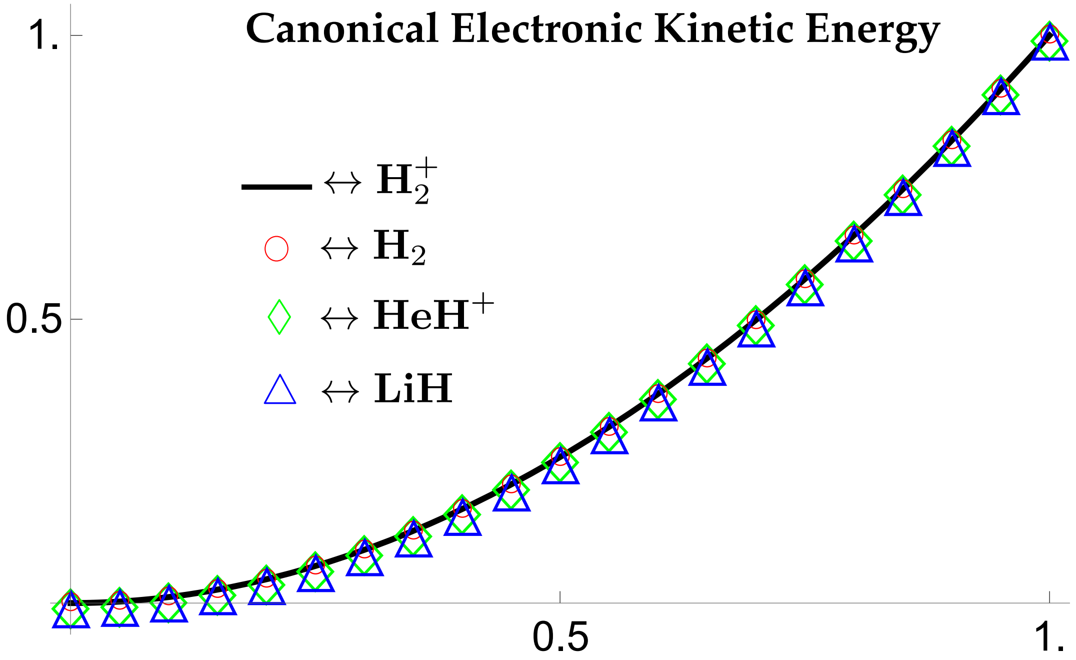
Generated adiabatic potential energy surface of OC-BrCl.



Pointwise relative errors on the estimated surface of OC-BrCl.

The multi-dimensional potential energy functions in Ar-HBr, Ar-HI, OC-HI, OC-HF, and OC-BrCl can be canonically transformed to a common dimensionless potential that is indicative of commonality in the potential energy functions of these differing categories of intermolecular interactions.

The Virial Theorem Functions

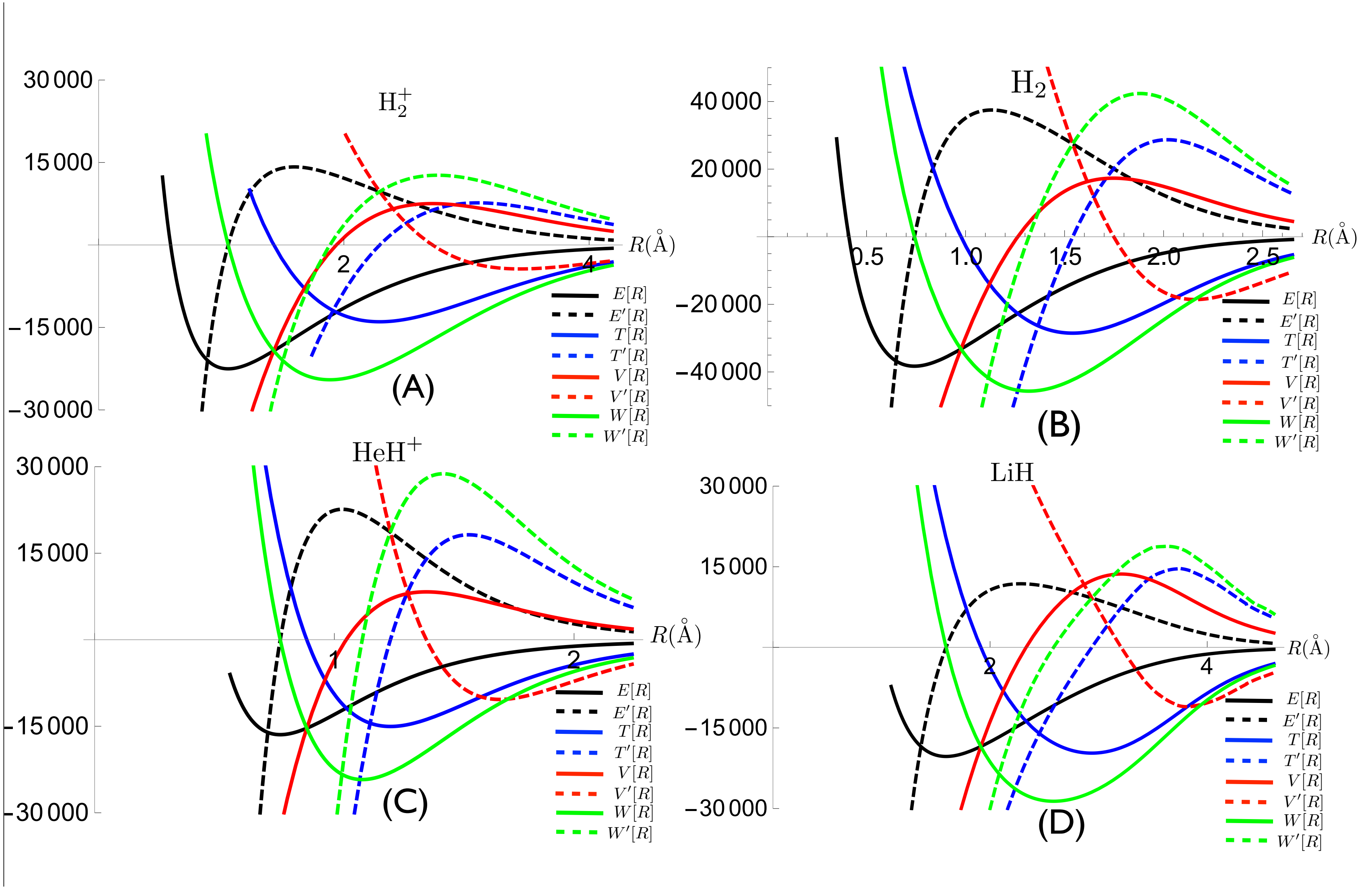


For Diatomic molecules:
2T = RF – V

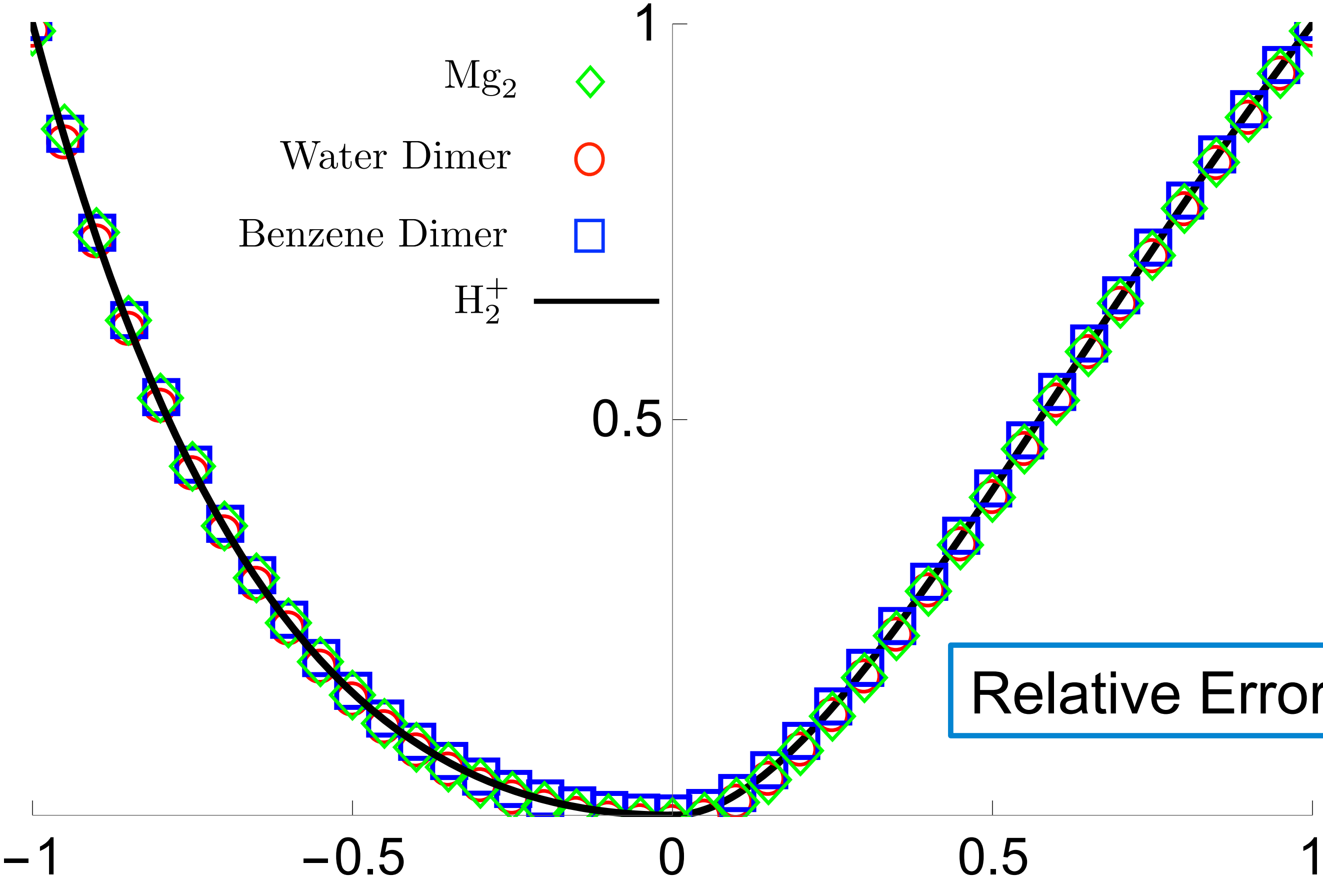
J. C. Slater, J. Chem. Phys. 1 (1933) 687.

Walton et al. J. Phys. Chem. A 120 (2016) 817.

The Virial Theorem Functions



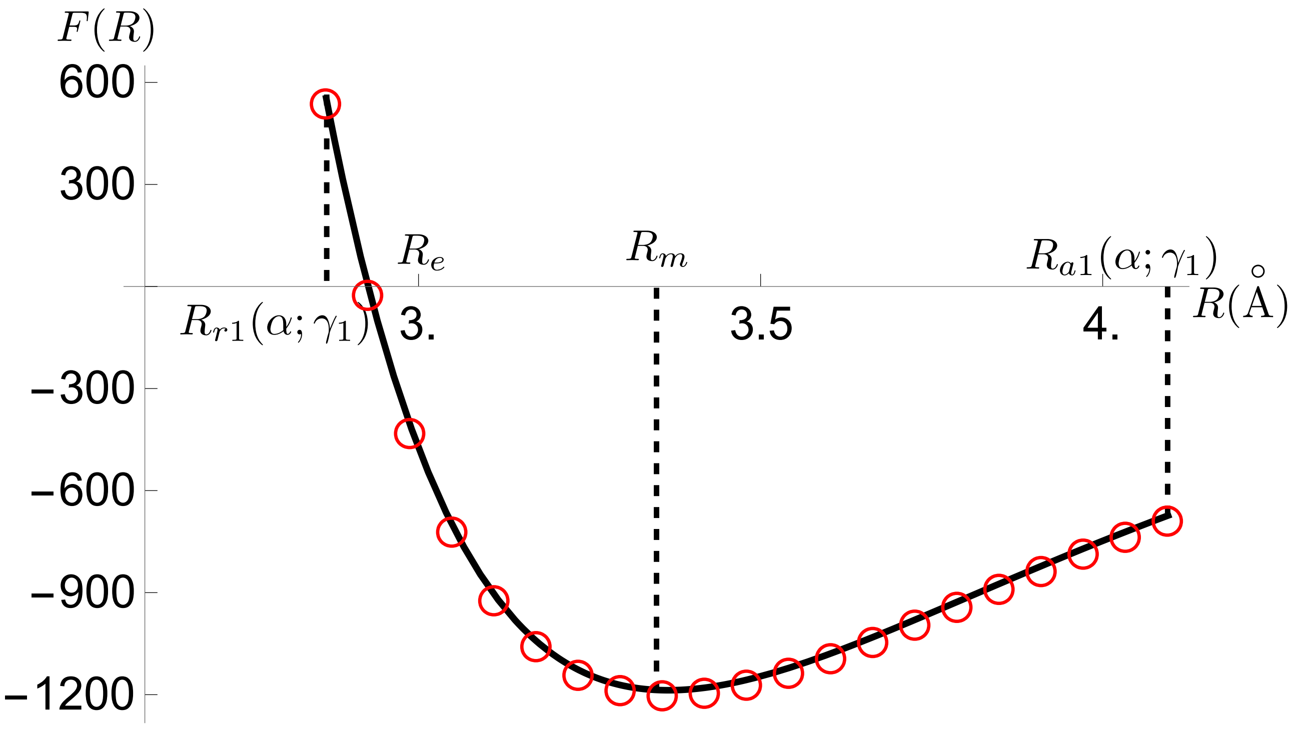
Canonical Feynman Force



Relative Errors < 0.8%

Walton et al. Chem. Phys. 474 (2016) 52.

Canonical Feynman Force



True radial force distribution for water dimer (solid curve) vs. approximation using force distribution for H_2^+ (red circles); the relative error is 0.0015.

Origin of the Canonical Transformations

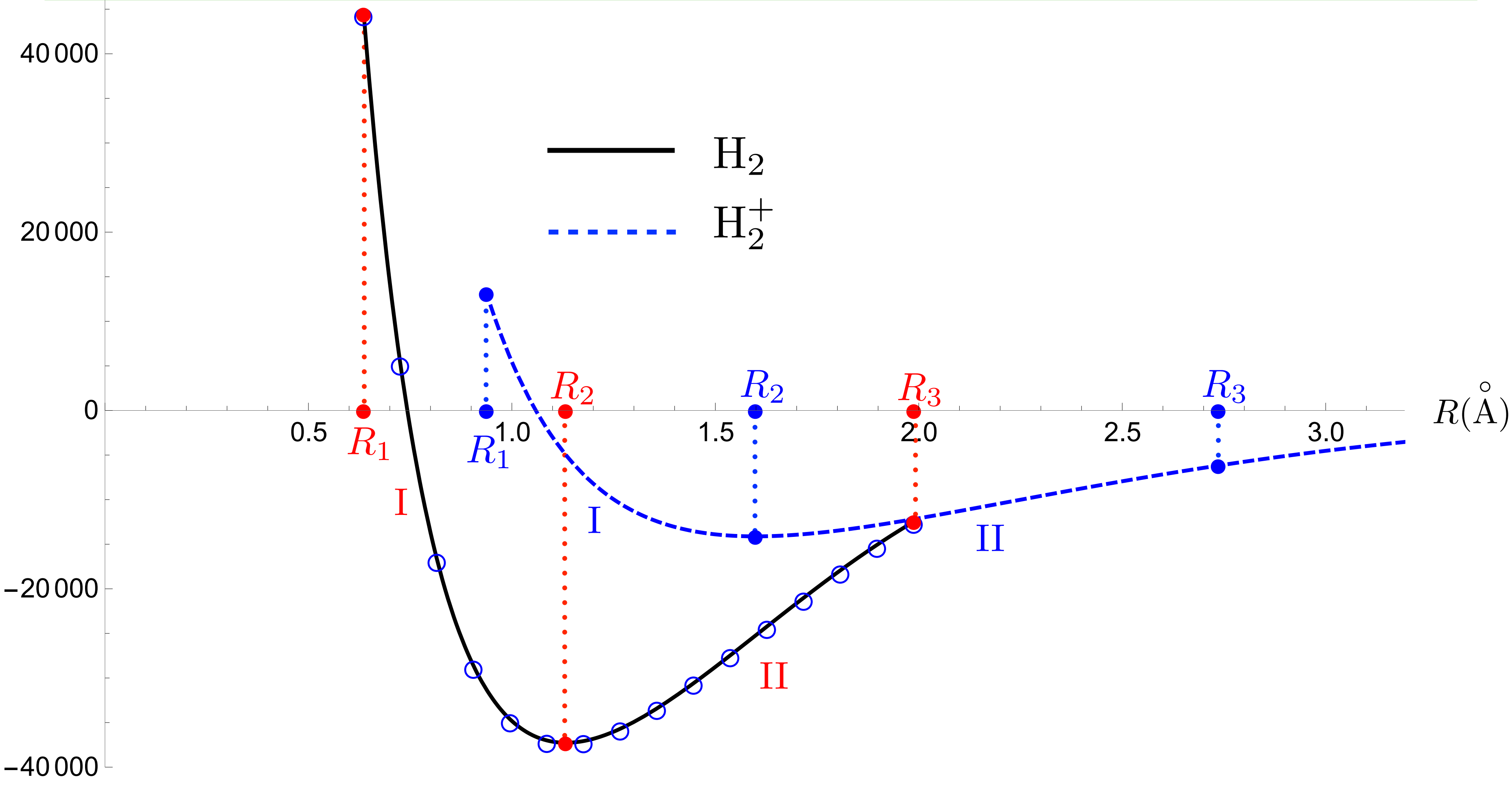
- If the force is canonical it implies that the potential is also canonical.
- However, the reverse implication is false in general.
- Why is the force canonical?
- Is the integral of the Hellmann-Feynman Theorem canonical?

$$F(R) = -\left\langle \psi \left| \frac{\partial H}{\partial R} \right| \psi \right\rangle = -\int \psi^* \frac{\partial H}{\partial R} \psi \, dv$$

For H_2 and H_2^+

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

Feynman force for H_2 constructed from the Feynman force curve for H_2^+ using the inverse canonical transformation.



Relative Errors: I) 0.00221; II) 0.00243

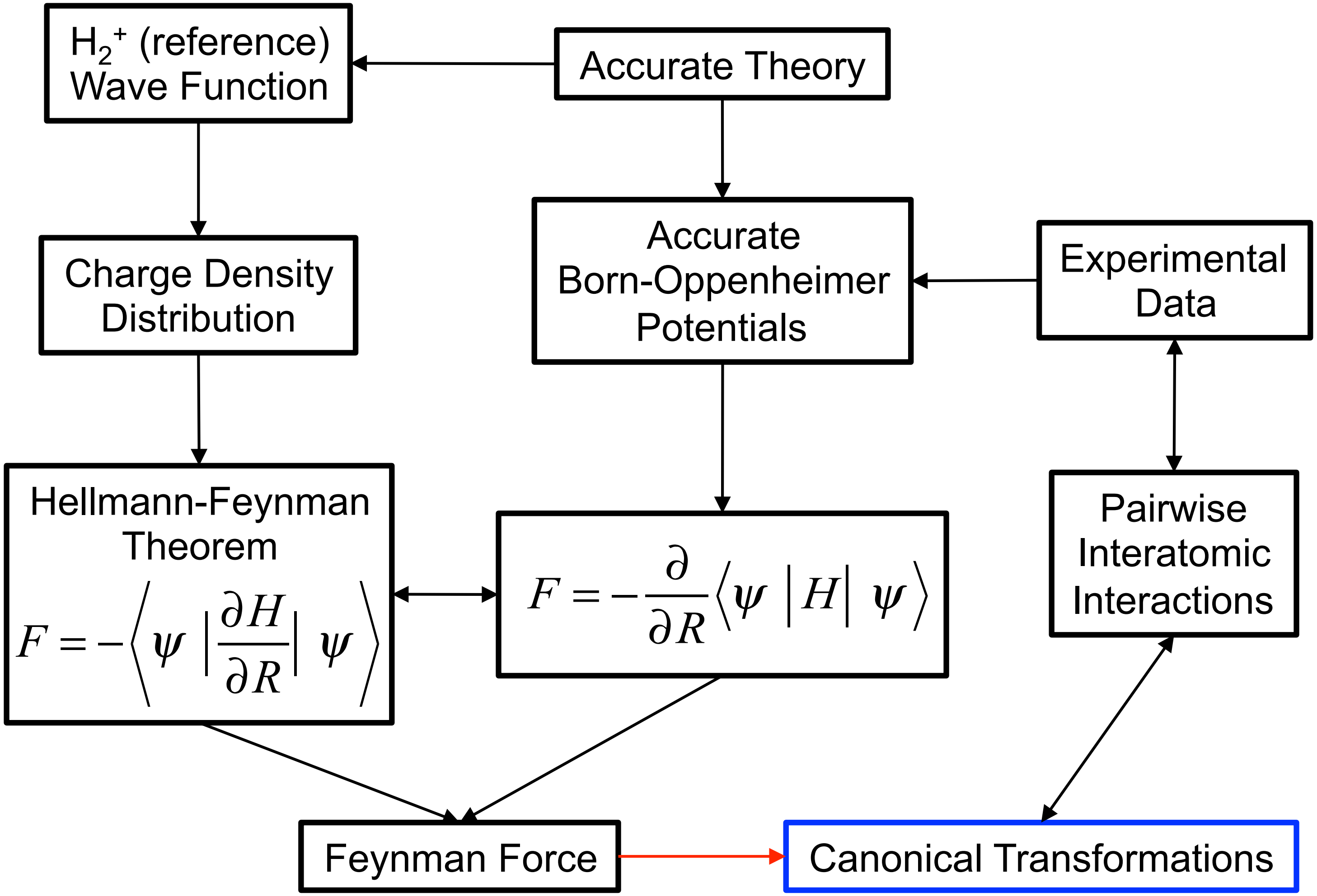
Origin of the Canonical Transformations

- Is the charge density canonical?

$$F(R) = -\left\langle \psi \left| \frac{\partial H}{\partial R} \right| \psi \right\rangle = -\int \psi^* \frac{\partial H}{\partial R} \psi \, dv$$

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

For H_2 and H_2^+



H_2^+ (reference) Wave Function

Accurate Theory

Charge Density Distribution

Accurate Born-Oppenheimer Potentials

Experimental Data

Hellmann-Feynman Theorem

$$F = -\left\langle \psi \left| \frac{\partial H}{\partial R} \right| \psi \right\rangle$$

$$F = -\frac{\partial}{\partial R}\left\langle \psi \left| H \right| \psi \right\rangle$$

Pairwise Interatomic Interactions

Feynman Force

Canonical Transformations

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

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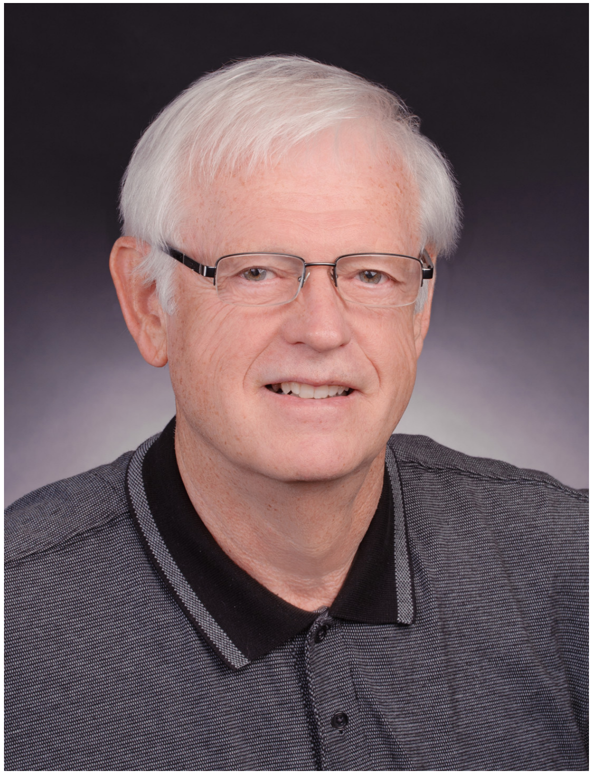

John W. Bevan, 70, passed away April 23, 2016 in Bryan, TX, USA. He was Professor of Chemistry and Davidson Professor of Science at Texas A&M University.

Bevan's main research involved molecular spectroscopy. His work was careful, thorough and complete. He was especially concerned with accuracy. His experimental work was centered on the investigation of weakly bound complexes to determine their properties, particularly intermolecular potential energy functions.

John Bevan was a caring, gentle, and humble person, greatly respected by students and colleagues alike.