3.5: The H2 Covalent Bond and the Virial Theorem

$$\text{Total energy:} \qquad E(R) = T(R) + V(R)$$

$$\text{Virial theorem:} \qquad 2T(R) + V(R) = -R\tfrac{d}{dR}E(R)$$

$$\text{Morse parameters:} \qquad D_e = 0.761 aJ \qquad \beta = 0.0193 pm^{-1} \qquad R_e = 74.1 pm$$

These parameters are taken from Fig. 5.6 on page 165 of McQuarrie and Simon's *Physical Chemistry: A Molecular Approach.*

$$\text{Morse Function:} \qquad E(R) = D_e \left[1 - \exp\left[-\beta\left(R - R_e\right)\right]\right]^2 - D_e$$

Using equation (1) to eliminate V(R) in equation (2) yields an equation for kinetic energy as a function of the internuclear separation.

$$\text{Kinetic energy:} \qquad T(R) = -E(R) - R\tfrac{d}{dR}E(R)$$

Using equation (1) to eliminate T(R) in equation (2) yields an equation for potential energy as a function of the internuclear separation.

$$\text{Potential energy:} \qquad T(R) = 2E(R) + R\tfrac{d}{dR}E(R)$$

John C. Slater [*J.Chem. Phys.* **1933**, *1*, 687-691] used the virial theorem to analyze the chemical bond and was among the first to note the importance of kinetic energy in covalent bond formation. He wrote,
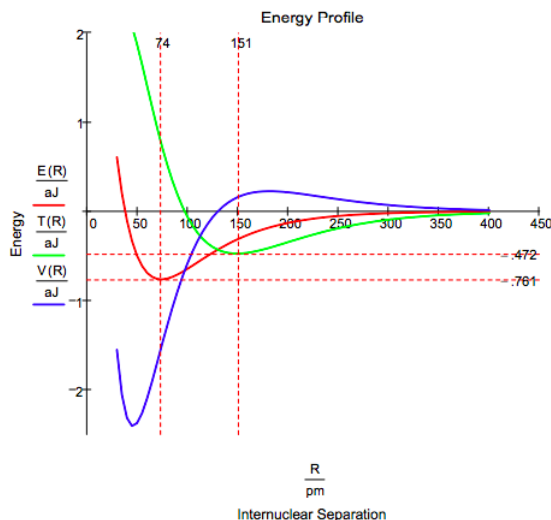
> ...this theorem gives a means of finding kinetic and potential energy separately for all configurations of the nuclei, as soon as the total energy is known, from experiment or theory.

> These important equations (4 and 5) determine the mean kinetic and potential energies as functions of R, one might almost say experimentally, directly from the curves of E as a function of R which can be found from band spectra. The theory is so simple and direct that one can accept the results without question....

John Winn [J. Chem. Phys. 1981, 74, 608-611] offered the following interpretation of the energy profile shown below.

> As the atoms approach, the potential energy rises (electrons are moving away from nuclei) and the kinetic energy falls (as delocalization begins). In the vicinity of R/Re = 2, this trend reverses. The kinetic energy increases as the wave function is localized ..., but the potential energy falls as the charge is now brought nearer both nuclei. Only at R/Re < 0.5 does nuclear repulsion cause the potential energy to increase and contribute to the total repulsion energy.

$$\text{Plot range:} \qquad R = 30pm,\ 35pm..400pm$$

The following table provides quantitative support for Winn's analysis.

$$\begin{pmatrix} o & \text{Step 1} & \text{Step 2} & \text{Overall} \\ \frac{\Delta T}{aJ} & -0.472 & 1.233 & 0.761 \\ \frac{\Delta V}{aJ} & 0.166 & -1.688 & -1.522 \\ \frac{\Delta E}{aJ} & -0.306 & -0.455 & -0.761 \\ \frac{R}{pm} & 151 & 74.1 & 74.1 \\ \text{Type} & \text{Molecular} & \text{Atomic} & \text{Molecular} + \text{Atomic} \end{pmatrix}$$

This type of analysis is valid for any diatomic molecule for which Morse paramters are available.

$$\text{Conversion factors:} \quad pm = 10^{-12}m \quad aJ = 10^{-18}joule$$