

3.7: Slater's Analysis of the Covalent Bond using the Virial Theorem

John C. Slater [*J. Chem. Phys.* **1933**, *1*, 687-691] used the virial theorem to analyze the chemical bond and was the first to recognize 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.

The kinetic energy, potential energy and total energy of the hydrogen molecule are calculated as a function of R using the virial theorem and a Morse function for the total energy based on experimental parameters.

Total energy:

$$E(R) = T(R) + V(R)$$

Virial theorem:

$$2T(R) + V(R) = -R \frac{d}{dR} E(R)$$

Morse parameters:

$$D_e = 0.761 \text{ aJ} \quad \beta = 0.0193 \text{ pm}^{-1} \quad R_e = 74.1 \text{ pm}$$

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

Morse function:

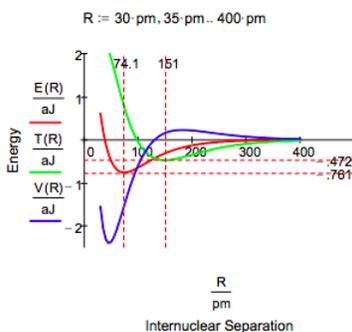
$$E(R) = D_e [1 - \exp[-\beta(R - R_e)]]^2 - D_e$$

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

$$T(R) = -E(R) - R \frac{d}{dR} E(R)$$

$$V(R) = 2E(R) + R \frac{d}{dR} E(R)$$

These important equations 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....



The covalent bond in H₂ can be thought of as arising from the overlap of 1s atomic orbitals forming a molecular orbital. As the atoms approach, the potential energy rises because constructive interference of the overlapping atomic orbitals draws electron density away from the nuclear centers into the bond region. Kinetic energy decreases due to delocalization of the electrons over the entire molecular orbital. At an inter-nuclear separation of 151 pm this trend reverses as the atomic orbitals shrink bringing electron density closer to both nuclei. It is the sharp increase in kinetic energy at 74.1 pm due to the shrinking of the molecular orbital that causes the energy minimum and the formation of a stable bond; potential energy is still in a steep decline and doesn't begin to

increase (mainly due to nuclear repulsion) until 40 pm. This analysis is based in part on a paper by John Winn [*J. Chem. Phys.* **1981**, 74, 608-611].

The following table provides quantitative support for Winn's analysis. Step 1 occurs from large inter-nuclear separation to 151 pm and is molecular in character. Step 2 is the change from 151 pm to 74.1 pm and is basically atomic as electron density is drawn closer to the nuclei and out of the inter-nuclear bond region.

		Step 1	Step 2	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
Type		Molecular	Atomic	Molecular + Atomic

Conversion factors:

$$pm = 10^{-12}m \quad aJ = 10^{-18}joule$$

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