Potential Energy Surfaces

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Potential Energy Surfaces

A *potential energy surface* is a mathematical function that gives the energy of a molecule as a function of its geometry.

- *Molecular Mechanics* provides this energy as a function of stretches, bends, torsions, etc. This is an approximate model that breaks down in some situations (e.g., breaking bonds). Only works when parameters are available.

- *Quantum Mechanics* provides an energy function which can be exact in principle and works for any molecule. In practice, approximate quantum methods are used due to computational expense.

The Molecular Hamiltonian

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_A \frac{1}{2M_A}\nabla_A^2 - \sum_{A,i}\frac{Z_A}{r_{Ai}} + \sum_{A>B}\frac{Z_A Z_B}{R_{AB}} + \sum_{i>j}\frac{1}{r_{ij}}, \tag{1}$$

in atomic units, where i, j refer to electrons and A, B refer to nuclei.

The Hamiltonian may be written more compactly as

$$\hat{H} = \hat{T}_N(\mathbf{R}) + \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}, \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r}), \tag{2}$$

where **R** is the set of nuclear coordinates and **r** is the set of electronic coordinates.

Separability

Some parts of the Hamiltonian depend on nuclear coordinates **R**, and others depend on electronic coordinates **r**. Any time the Hamiltonian is separable like

$$\hat{H}(q_1, q_2) = \hat{H}_1(q_1) + \hat{H}_2(q_2), \tag{3}$$

then the eigenfunctions are just

$$\Psi(q_1, q_2) = \Psi_1(q_1)\Psi_2(q_2) \tag{4}$$

and the eigenvalues are just $E = E_1 + E_2$, where $\hat{H}_1(q_1)\Psi_1(q_1) = E_1\Psi_1(q_1)$ and $\hat{H}_2(q_2)\Psi_2(q_2) = E_2\Psi_2(q_2)$. Unfortunately, the electron-nuclear potential energy $\hat{V}_{eN}(\mathbf{r}, \mathbf{R}) = -\sum_{A,i} \frac{Z_A}{r_{Ai}}$ prevents our molecular Hamiltonian from being separable.

The Born-Oppenheimer Approximation

Try to separate the electronic and nuclear degrees of freedom even though they are coupled by the electron-nuclear potential energy $\hat{V}_{eN}(\mathbf{r}, \mathbf{R})$. We can do this because the electrons are much lighter than the nuclei, and so with respect to the electrons, the nuclei are almost stationary. Thus we

1. Fix the nuclei at some chosen configuration $\mathbf{R}_a$
2. Solve for the motion of the electrons for this nuclear configuration, giving an electronic energy $E_e(\mathbf{R}_a)$ and wavefunction $\Psi(\mathbf{r}; \mathbf{R_a})$
3. Repeat for other nuclear configurations $\mathbf{R_b}$ of interest, building up a *Potential Energy Surface* $E_e(\mathbf{R})$.

Some Mathematical Details

Initially, $\hat{T}_N(\mathbf{R})$ can be neglected since $\hat{T}_N$ is smaller than $\hat{T}_e$ by a factor of M_A/μ_e, where μ_e is the reduced mass of an electron. Thus for a *fixed* nuclear configuration, we have

$$\hat{H}_{el} = \hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r};\mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r}) \tag{5}$$

such that

$$\hat{H}_e(\mathbf{r};\mathbf{R})\Psi(\mathbf{r};\mathbf{R}) = E_e(\mathbf{R})\Psi(\mathbf{r};\mathbf{R}) \tag{6}$$

This is the "clamped-nuclei" Schrödinger equation. Note $\hat{V}_{NN}(\mathbf{R})$ is just a constant for any particular $\mathbf{R}$.

The Total Wavefunction

An exact solution to the full Schrödinger equation can be obtained by using an (infinite) expansion of the form

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_k \Psi_k(\mathbf{r}; \mathbf{R}) \chi_k(\mathbf{R}), \tag{7}$$

although usually only one or two terms are necessary for a particular state. Inserting this expansion into the original Schrödinger equation eventually yields:

$$\begin{aligned} \left[\hat{T}_N + \hat{T}'_{kk} + T''_{kk} + U_{kk} - E\right] \chi_k(\mathbf{R}) &= \\ -\sum_{k' \neq k} \left[U_{kk'} + \hat{T}'_{kk'} + T''_{kk'}\right] \chi_{k'}(\mathbf{R}) \end{aligned} \tag{8}$$

where

$$\hat{T}_N = -\sum_A \frac{1}{2M_A} \nabla_A^2, \tag{9}$$

$$\hat{T}'_{kk'}(\mathbf{R}) = \sum_A \frac{-1}{M_A} \langle \Psi_k(\mathbf{r};\mathbf{R}) | \nabla_A | \Psi_{k'}(\mathbf{r};\mathbf{R}) \rangle \cdot \nabla_A, \tag{10}$$

$$T''_{kk'}(\mathbf{R}) = \sum_A \frac{-1}{2M_A} \langle \Psi_k(\mathbf{r};\mathbf{R}) | \nabla_A^2 | \Psi_{k'}(\mathbf{r};\mathbf{R}) \rangle, \tag{11}$$

$$U_{kk'}(\mathbf{R}) = \langle \Psi_k(\mathbf{r};\mathbf{R}) | \hat{H}_e | \Psi_{k'}(\mathbf{r};\mathbf{R}) \rangle. \tag{12}$$

The Nuclear Wavefunction

Fortunately, the previous expressions involve terms which are usually small, and assuming the wavefunction is real, we normally obtain the following equation for the motion of the nuclei on a given Born-Oppenheimer potential energy surface:

$$\left[\hat{T}_N + T''_{kk} + U_{kk}\right] \chi_k(\mathbf{R}) = E \chi_k(\mathbf{R}) \tag{13}$$

Thus, when the off-diagonal couplings can be ignored, the nuclei move in a potential field set up by the electrons. The potential energy at each point is given primarily by U_{kk} (the expectation value of the electronic energy, just $E_e(\mathbf{R})$ previously), with a small correction factor T''_{kk}, called the *Born-Oppenheimer Diagonal Correction* (BODC).

The Born-Oppenheimer Diagonal Correction

$$E_{BODC} = \langle \Psi(\mathbf{r};\mathbf{R}) | \hat{T}_n | \Psi(\mathbf{r};\mathbf{R}) \rangle, \tag{14}$$

Also called the *adiabatic correction.* First systematic study at the Hartree-Fock level by Handy, Yamaguchi, and Schaefer (1986). First systematic study at correlated levels of theory by Valeev and Sherrill (2003).

Table 1: Adiabatic correction to the barrier to linearity of water in the ground state (in cm^{-1})[a]

Basis	Method	C_{2v}	$D_{\infty h}$	ΔE_e[b]
cc-pVDZ	RHF	600.28	585.20	-15.08
cc-pVDZ	CISD	615.03	599.15	-15.88
cc-pVDZ	CISDT	616.82	600.62	-16.20
cc-pVTZ	RHF	596.53	581.43	-15.10
cc-pVTZ	CISD	611.89	596.73	-15.16
cc-pVQZ	RHF	595.57	580.72	-14.85

[a] Data from Valeev and Sherrill, 2003.

[b] The difference between the adiabatic correction for the C_{2v} and $D_{\infty h}$ structures.

Table 2: Adiabatic corrections to bond length and harmonic frequencies of BH, CH^+, and NH[a]

	BH	CH^+	NH
Δr_e (Å)	0.00066	0.00063	0.00027
$\Delta \omega_e$ (cm^{-1})	-2.25	-2.81	-1.38

[a] Data from Temelso, Valeev, and Sherrill, 2004.

Coordinates for Potential Energy Surfaces

In the absence of fields, a molecule's potential energy doesn't change if it is translated or rotated in space. Thus the potential energy only depends on a molecule's *internal coordinates*. There are $3N$ total coordinates for a molecule (x, y, z for each atom), minus three translations and three rotations which don't matter (only two rotations for linear molecules). The internal coordinates may be represented by simple stretch, bend, torsion coordinates, or symmetry-adapted linear combinations, or redundant coordinates, or normal modes coordinates, etc.

Characterizing Potential Energy Surfaces

The most interesting points on PES's are the *stationary points*, where the gradients with respect to all internal coordinates are zero.

1. Minima: correspond to stable or quasi-stable species; i.e., reactants, products, intermediates.
2. Transition states: saddle points which are minima in all dimensions but one; a maximum in that dimension.
3. Higher-order saddle points: a minimum in all dimensions but n, where $n > 1$; maximum in the other n dimensions.

Figure 1: Example PES from Steinfeld, Francisco, and Hase

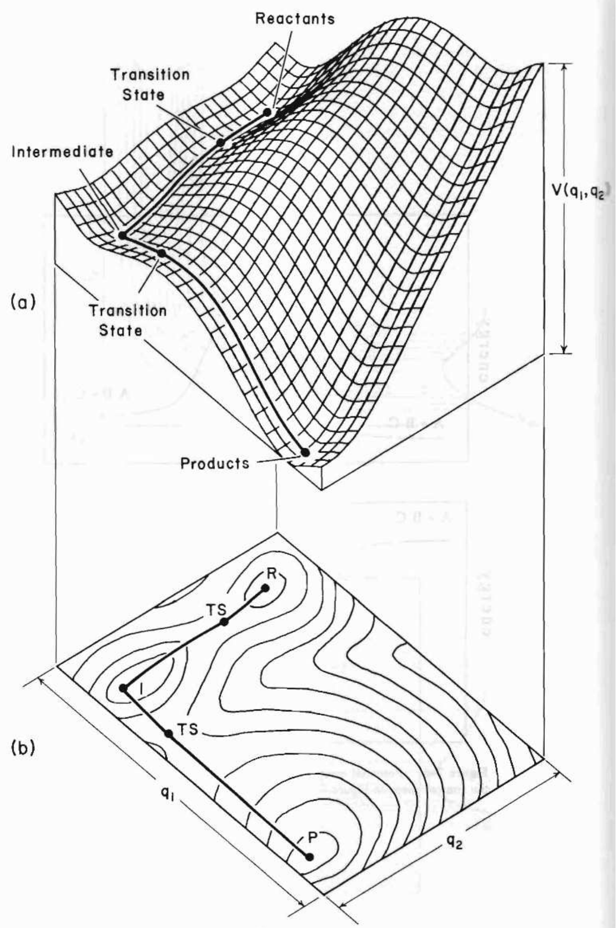
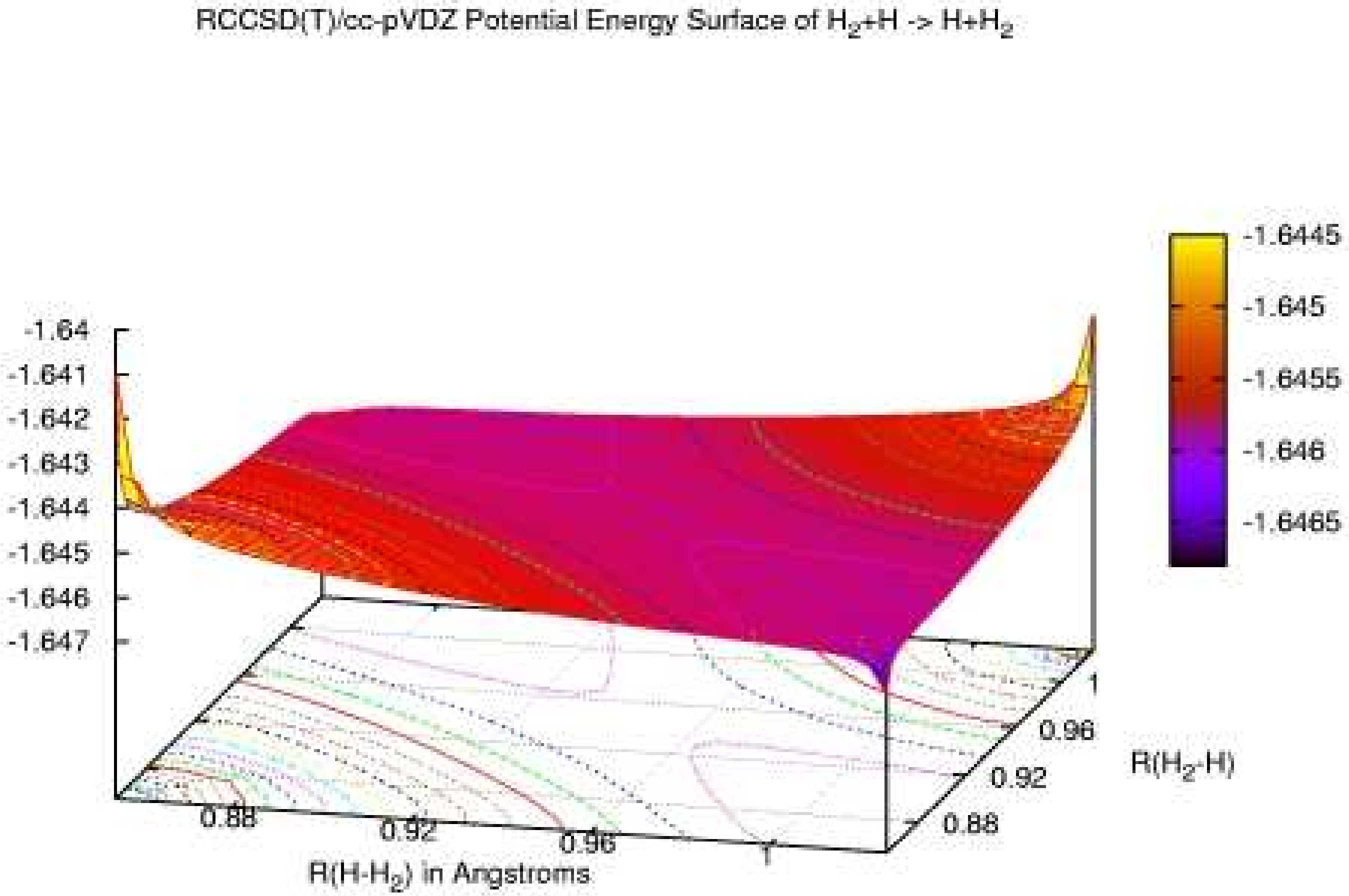


Figure 7–7. A three-dimensional perspective (a) and contour map (b) for a model chemical reaction. The solid line is the reaction path. [Adapted from G. M. Maggiora and R. E. Christofferson, in *Transition States of Biochemical Processes*, ed. R. D. Gandour and R. L. Schowen (New York: Plenum, 1978).]

Figure 2: $H_2 + H \rightarrow H + H_2$



Hessian Index

The *Hessian index* is the number of negative eigenvalues of the force constant matrix. For a stationary point, this corresponds to the number of internal degrees of freedom along which that point is a potential energy maximum. The Hessian index is 0 for minima, 1 for transition states, > 1 for higher-order saddle points. The Hessian index also corresponds to the *number of imaginary vibrational frequencies.*

A geometry optimization, when run to completion, will provide a stationary point geometry. Typically, this is a potential energy minimum. However, the optimization might get stuck on a saddle point. A vibrational analysis can verify the nature of the stationary point via the Hessian index.