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# ENERGETIC PRINCIPLES OF CHEMICAL REACTIONS



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Preface

This text is intended for a one-quarter or one-semester course at the first- or second-year graduate level. It discusses how symmetry concepts, orbital nodal patterns, and molecular topology can be used to make statements about energetics in chemical reactions. It also differs from commonly used texts that only consider how orbital-symmetry constraints allow or forbid various reactions in its more rigorous approach. Introductory chapters explain the physical origins of orbital-, configuration-, and state-correlation diagrams, Jahn-Teller instability, internal conversion, and intersystem crossing. These sections are for students who desire a rigorous understanding of the physical origins of these concepts as they relate to thermal and photochemical processes. These discussions are not unduly long, however, and they contain sufficient physical interpretations to make them valuable reading for graduate students and researchers in all areas of chemistry. Following the introduction of the physical principles, applications to explicit thermal and photochemical reaction problems show the practical uses of these tools. These examples, which are written in a tutorial style, should appeal to all students of chemistry.

Most one-semester introductory courses on quantum chemistry and twoquarter combined courses on quantum chemistry and spectroscopy should provide adequate background to understand the material in this text. Some concepts of group theory also appear; more advanced topics are taught in the text as needed. General ideas of Hartree-Fock molecular orbital theory sometimes come into use, but only to the extent that they are absolutely necessary. Little is said about numerical application of molecular orbital methods; instead, emphasis is placed on the conceptual use of orbitals and their symmetries in chemical reactions. Three appendixes are provided for the reader to review or to learn the requisite background material dealing with *ab initio* molecular theory, molecular-point-group symmetry methods, and the photon absorption process that prepares molecular reactants for subsequent photoreaction. For the reader who wishes to test his or her mastery of the material, two sets of problems are provided.

This text is the result of a one-quarter graduate course taught to first-year graduate students in physical, organic, and inorganic chemistry at the Univer-

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### ENERGETIC PRINCIPLES OF CHEMICAL REACTIONS

## Part 1 Underlying Physical Principles

In the first three chapters of this text we show how to express, in quantitative terms, certain concepts that are widely used in a qualitative manner in chemical education and research. Specifically, we analyze how one defines potential energy surfaces and reaction coordinates, and we examine the conditions under which these concepts break down. By observing how the reaction coordinate varies as the reaction proceeds from reactants, through one or more transition states, to products, the idea of symmetry conservation is developed. In Chapter 3 we discuss the concepts of orbitals, electronic occupancies (configurations), and electronic states, and we show why symmetry conservation applies at each of these three levels.

The ultimate goal of this text is to permit the reader to predict whether any postulated chemical reaction should experience a large activation energy barrier and, thereby, be forbidden. To make such predictions, one must be able to visualize the reactant molecules moving on a potential energy surface that is characteristic of either the ground state or an excited electronic state. Such qualitative visualization can be carried out only after one has achieved a good appreciation of the electronic structures (i.e., orbital shapes and energies, and orbital occupancies) of the reactants, products, and likely transition states. The first three chapters of this text develop these important tools.

The level of presentation in these first three chapters is substantially more sophisticated than in most other books that deal with symmetry in chemical reactions (for example, Pearson, 1976; Woodward and Hoffmann, 1970; Borden, 1975; or Fleming, 1976). This level is especially relevant to physical chemists whose research requires a *quantitative* interpretation of experimental data—modern research in chemical dynamics and spectroscopy often demands the use of such theoretical tools. Likewise, it is important also that researchers who wish to make qualitative use of symmetry ideas be aware of the origins and limitations of such concepts. Therefore, although the vast majority of the examples treated in later chapters make only qualitative use of the theoretical machinery covered in Chapters 1–3, it is essential that all modern researchers be well founded in the physical origins of these valuable symmetry tools. It is recommended that readers who are not familiar with the foundations of molecular orbital theory and point-group symmetry read Appendixes A and C before attempting to master these first three chapters.

### Chapter 1

### **Potential Energy Surfaces**

As will become clear shortly, a potential energy surface is merely a construct of one's imagination. It is an idea that has proved to be of immense value for conceptualizing chemical reactions but that loses its rigorous content in certain circumstances. Within its range of approximate validity, a potential energy surface can be thought of as the topographical map describing the terrain on which the reactant molecules must move on their route to a transition state and then onward toward the geometrical arrangement of the product molecules. To understand better what these potential energy surfaces are, it is useful to examine how they arise in the quantum mechanical treatment of the motions of the nuclei and the electrons that comprise the reactant molecules.

The Hamiltonian function describing motion of a collection of nuclei of masses  $M_a$  and charges  $Z_a e$  and electrons of mass m and charge -e is

$$H = \sum_{a} \left[ -\frac{\hbar^2}{2M_a} \nabla_a^2 + \frac{1}{2} \sum_{b \neq a} \frac{Z_a Z_b e^2}{|\mathbf{R}_a - \mathbf{R}_b|} \right] + \sum_{i} \left[ -\frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \sum_{j \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{a} \frac{Z_a e^2}{|\mathbf{r}_i - \mathbf{R}_a|} \right], \quad (1.1)$$

where  $(\mathbf{R}_a, \mathbf{r}_i)$  refers to a coordinate system that is fixed in space and not on the molecule.

It is convenient to rewrite the Hamiltonian in terms of molecule-fixed coordinates instead of absolute coordinates. Two such coordinate transformations might be used. First, one could introduce the *total* center of mass

$$\mathbf{R} = \frac{1}{M} \left[ \sum_{a} M_{a} \mathbf{R}_{a} + \sum_{i} m \mathbf{r}_{i} \right],$$

in which M is the total mass of all nuclei and electrons and coordinates relative to **R**. This is a good and natural choice but one that is not convenient once the

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idea of clamped nuclei, which we will use repeatedly, is introduced. If the nuclei are held fixed and the electrons move, the center of mass, which is the coordinate origin, could move; as a result, what was ascribed to electronic motion would include some center-of-mass motion. As will become clear shortly, our desire to think of the nuclei as fixed is important; the clamped-nuclei concept rests at the center of our ideas of potential energy surfaces.

A second transformation uses the center of mass of the nuclei to define a molecule-fixed coordinate origin

$$\mathbf{R} = \frac{1}{M} \sum_{a} M_{a} \mathbf{R}_{a}; M = \sum_{a} M_{a}.$$

Because the electrons are so light, this position will almost be the true center of mass, and this location will remain fixed if we later clamp the nuclei. Upon expressing the positions of the nuclei and electrons as **R** plus internal or relative position vectors (for which we now use  $\mathbf{R}_a$ ,  $\mathbf{r}_i$ ), the above Hamiltonian can be written, for a diatomic molecule,

$$H = \sum_{i} \left[ \left( \frac{-\hbar^2}{2m} \nabla_i^2 \right) - \sum_{a} \frac{Z_a e^2}{|\mathbf{r}_i - \mathbf{R}_a|} + \frac{1}{2} \sum_{j \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right] + \frac{Z_a Z_b e^2}{|\mathbf{R}_a - \mathbf{R}_b|} - \frac{\hbar^2}{2\mu} \nabla_{|\mathbf{R}_a - \mathbf{R}_b|}^2 - \frac{\hbar^2}{2M} \sum_{i,j} \nabla_i \cdot \nabla_j - \frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2 \qquad (1.2)$$

in which  $\mu$ , the reduced mass of the nuclei is  $M_a M_b/M$ . Pack and Hirschfelder (1967) show the details of how both this transformation and the total-centerof-mass transformation mentioned above are carried out. For a more complicated molecule, only the fourth and fifth terms would differ; the fourth would be

$$\frac{1}{2}\sum_{a,b}\frac{Z_aZ_be^2}{|\mathbf{R}_a-\mathbf{R}_b|}$$

and the fifth would be the internal kinetic energy operator, which we label  $h_N$ , describing the vibrations and rotations of the nuclei. As an example, consider a triatomic molecule ABC. For such a molecule 3N-3 = 6 such coordinates are needed, and these could be the vectors  $\mathbf{R}_C - \mathbf{R}_B$  and  $\mathbf{R}_A - \mathbf{R}_B$  or the lengths  $|\mathbf{R}_C - \mathbf{R}_B|$ ,  $|\mathbf{R}_A - \mathbf{R}_B|$ , and the angle  $\theta_{ABC}$  and three Euler orientation angles. The choice is up to you and should be made to simplify the treatment of the vibration/rotation problem, which Wilson, Decius, and Cross (1955) treat in elegant detail. The seventh term in equation 1.2, the motion of the nuclear

center of mass, separates exactly. Hence, this motion is uncoupled from the internal electronic and vibration/rotation motion and will therefore be assumed to have been removed from further consideration (by separation of variables).

The first four terms and the sixth term in equation 1.2 are usually combined and called the electronic Hamiltonian  $(h_e)$  because they contain differential operators only for the  $\mathbf{r}_i$  coordinates. Notice that the electronic energy will then contain the repulsion of the nuclei, so the potential energy curves will become infinitely repulsive as two nuclei approach one another. The sixth term, sometimes called the mass-polarization term, usually has small effects because it is multiplied by the inverse of the total nuclear mass M (a small factor) in contrast with the electronic kinetic energy term, which has a  $h^2/2m$ multiplier (a large factor). Hence, it is common (but not necessary) to ignore this term in writing  $h_e$ . See Pack and Hirschfelder (1968) for further justification of this idea.

In seeking eigenstates  $\psi$  of  $H = h_e + h_N$ , it is usual to introduce the eigenfunctions of  $h_e$  as a basis for expressing the  $\mathbf{r}_i$  dependence of  $\psi$ . What does this mean? Since  $h_e$  is a Hermitian operator in  $\mathbf{r}_i$  space (which also contains reference to the locations of the nuclei), the eigenfunctions  $\phi_k$  of  $h_e$ 

$$h_{\epsilon}(\mathbf{r}_{i} | \mathbf{R}_{a})\phi_{k}(\mathbf{r}_{i} | \mathbf{R}_{a}) = E_{k}(\mathbf{R}_{a})\phi_{k}(\mathbf{r}_{i} | \mathbf{R}_{a})$$
(1.3)

form a complete set of functions of  $\mathbf{r}_i$ . Note that  $h_e$  depends on  $\mathbf{R}_a$  even though it is not an *operator* in the  $\mathbf{R}_a$  space. Hence, the  $E_k$  and  $\phi_k$  will vary as  $\mathbf{R}_a$ varies. However, for any specific  $\mathbf{R}_a$ , the set of  $\{\phi_k\}$  is complete in  $\mathbf{r}_i$  space. Hence, because it describes motion of electrons and nuclei, the *total* wave function  $\psi$ , which depends on  $\mathbf{r}_i$  and  $\mathbf{R}_a$ , can be expanded to yield

$$\psi(\mathbf{r}_i, \mathbf{R}_a) = \sum_k \phi_k(\mathbf{r}_i | \mathbf{R}_a) \chi_k(\mathbf{R}_a)$$
(1.4)

in which, for now, the  $\chi_k(\mathbf{R}_a)$  can be viewed as "expansion coefficient functions" that are to be determined from the equation  $H\psi = E\psi$ .

Substituting the expression for  $\psi$  in equation 1.4 into the *total* Schrödinger equation, premultiplying by  $\phi_i^*(\mathbf{r}_i | \mathbf{R}_a)$ , and integrating over the *electronic* coordinates  $\{\mathbf{r}_i\}$ , we obtain for a diatomic molecule (analysis of polyatomic molecules is more tedious but gives rise to no new features)

$$\sum_{k} \int (\phi_{l}^{*} [h_{e} \phi_{k} \chi_{k} - E \phi_{k} \chi_{k} - \frac{\hbar^{2}}{2\mu} (\phi_{k} \nabla_{R}^{2} \chi_{k} + \chi_{k} \nabla_{R}^{2} \phi_{k} + 2 \nabla_{R} \phi_{k} \cdot \nabla_{R} \chi_{k})] d\mathbf{r}_{1} d\mathbf{r}_{2} \dots d\mathbf{r}_{N} = 0$$

$$(1.5)$$

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in which the symbol R is now used for the internuclear distance  $R = |R_a - R_b|$ . Recall that the center-of-mass motion has been removed. Using equation 1.3 and the orthonormality of the  $\{\phi_k\}$ , this equation reduces to

$$\begin{bmatrix} E_l - E - \frac{\hbar^2}{2\mu} \nabla_R^2 \end{bmatrix} \chi_l = + \sum_k \left[ \int \phi_l^* \nabla_R^2 \phi_k \, d\mathbf{r} \chi_k \, \frac{\hbar^2}{2\mu} \right] + 2 \, \frac{\hbar^2}{2\mu} \int \phi_l^* \nabla_R \phi_k d\mathbf{r} \cdot \nabla_R \chi_k \end{bmatrix}.$$
(1.6)

The primary fact to notice in equation 1.6 is that there is *coupling* between the electronic states  $\phi_k$  and  $\phi_l$  caused by the fact that  $\phi_k$  and  $\phi_l$  depend upon  $\mathbf{R}_a$  and, hence, vary as  $\mathbf{R}_a$  moves. Thus, the  $\psi$  function of equation 1.4 cannot be expressed as a *single* product  $\phi_k \chi_k$  but requires all of the *electronic* wavefunctions to describe even a single *total* state wavefunction. Faced with the problem that it is not possible to express the exact solution as an electronic wavefunction multiplied by a vibration/rotation function, an approximation is needed. Two approximations are described in the following section.

### 1.1. Born-Oppenheimer and Adiabatic Approximations

In the Born-Oppenheimer approximation, all of the terms on the right-hand side of equation 1.6 (including the  $\phi_k = \phi_l$  term) are ignored. This procedure is equivalent to assuming that  $\psi$  can be approximated as  $\phi_l \chi_l$  and that  $\phi_l$  does not vary (strongly) with  $\mathbf{R}_a$ . Then, equation 1.6 is the Schrödinger equation for the motion (vibration/rotation) of the nuclei in the potential energy field  $E_l(\mathbf{R}_a) = V_l$ , namely,

$$\left(-\frac{\hbar^2}{2\mu}\nabla_{\rm R}^2+V_l\right)\chi_l=E\chi_l.$$
(1.7)

This equation states that the electronic energy, which certainly depends on where the nuclei are located, provides the potential energy surface on which the nuclei move. (Note that this potential surface is different for different electronic states labeled by *l*.) Thus, equation 1.7 is nothing but the vibration/rotation (V/R) problem and  $\chi_l$  is one of the V/R wavefunctions for the *l*th state. In other words,  $\chi_l = \chi_{l,vJ}$  and  $E = E_{l,vJ}$ ; v and J are the vibration and rotation quantum numbers.

In the adiabatic approximation, the k = l terms on the right-hand side of equation 1.6 are retained. As a result, the potential surface felt by the nuclei also includes the terms

$$\int \phi_i^* \left( -\frac{\hbar^2}{2\mu} \nabla_{\mathbf{R}}^2 \phi_i \right) d\mathbf{r} \qquad \text{and} \qquad \int \phi_i^* \left( -\frac{\hbar^2}{\mu} \nabla_{\mathbf{R}} \phi_i \right) d\mathbf{r} \cdot \nabla_{\mathbf{R}}.$$

The V/R wavefunctions  $x_i$  then also depend upon these "non-Born-Oppenheimer (BO) correction terms." Very few calculations in the literature have included such corrections. In the nonadiabatic approximation one attempts to keep all, or at least the most significant, terms in equation 1.6, but *ab initio* calculations at this level have been done only on very small systems (see Kolos and Wolniewicz, 1963, 1964, 1965).

Whenever we have two or more surfaces  $(E_1 \text{ and } E_2)$  that come close together, we *must* consider the coupling of their electronic and nuclear motions. The usual way to think of this is to assume that the two *unperturbed* problems (ignoring the right-hand side of equation 1.6) for  $\phi_1 \chi^0_{1,vJ}$  and  $\phi_2 \chi^0_{2,vJ}$ , have been solved. Then we attempt to represent the true  $\psi$  as a combination of these two most important terms with unknown coefficients. The resulting  $2 \times 2$ secular problem has diagonal elements  $E^0_{1,vJ}$  and  $E^0_{2,vJ}$ ; for specific choices of vJ and v'J' these elements can be nearly degenerate. The off-diagonal terms are

$$-\frac{\hbar^2}{2\mu}\left\langle\phi_1\chi^0_{1,\nu J}\big|(\nabla^2_{\mathsf{R}}\phi_2)\chi^0_{2,\nu' J'}+2(\nabla_{\mathsf{R}}\phi_2)\cdot\nabla_{\mathsf{R}}\chi^0_{2,\nu' J'}\right\rangle.$$

These non-Born-Oppenheimer coupling matrix elements, which determine the splitting between the two potential surfaces, will be large in regions of  $\mathbf{R}$ -space in which the electronic wavefunctions are expected to undergo large changes in their bonding characteristics (for example, when changing from ionic to covalent bonds or when breaking old bonds and forming new bonds).

Although it might not be important to be able to perform quantitative *ab initio* quantum calculations that include non-Born-Oppenheimer terms, it is important to *understand* when such terms are likely to be large, because it is under these circumstances that the concept of the separate or uncoupled potential energy surfaces ( $V_i$ ) breaks down. Alternatively, the idea of potential energy surfaces can be kept, and the coupling terms on the right-hand side of equation 1.6 can be viewed as giving rise to *transitions* from one surface to another. Such so-called *radiationless transitions* become important when the potential energy surfaces of the electronic states  $\phi_k$  and  $\phi_l$  approach or intersect one another. This problem of the rate of transitions among surfaces will be treated in more detail later (Chapters 5 and 6), when photochemical processes in which a molecule is prepared in an excited state are considered.

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### **1.2. Intersections of Potential Energy Surfaces**

In section 1.1 reference was made to electronic potential energy surfaces that intersect. Let us now briefly examine the circumstances in which two surfaces actually can "cross" one another. Consider a pair of approximate *electronic* wavefunctions  $\phi_1$  and  $\phi_2$  that might correspond to two different electronic configurations (e.g., Na<sup>+</sup>, Cl<sup>-</sup> and Na<sup>+</sup>, Cl<sup>-</sup>) of the same molecule. Alternatively, one could be referring to the coupling of zeroth-order Born-Oppenheimer wavefunctions to yield the full non-Born-Oppenheimer  $\psi$ , as discussed above. In the former case, the 2 × 2 secular problem that results from using these two functions as a basis for approximating the correct electronic wavefunctions  $\phi_1$ and  $\phi_2$  has energy levels given by the expression

$$E_{\pm} = \frac{1}{2} \left[ h_{11} + h_{22} \pm \sqrt{(h_{11} - h_{22})^2 + 4h_{12}^2} \right]$$
(1.8)

in which

$$h_{ij} = \int \phi_i^* h_e \phi_j \, d\mathbf{r}. \tag{1.9}$$

To make the two energy levels  $E_{+}$  equal (for surface intersection) it is necessary that  $h_{11} = h_{22}$  and  $h_{12} = 0$  at the same geometrical point(s). For a diatomic molecule, the elements  $h_{ii}$  are functions of R only, so it is not generally possible to find R-values at which both of the above conditions are met. As a result, potential energy curves of diatomic molecules do not cross (unless  $\phi_1$  and  $\phi_2$ have different symmetry and  $h_{12}$  is identically zero for all R). For a general molecule with N atoms, there are 3N - 5 (linear) or 3N - 6 (nonlinear) vibrational degrees of freedom upon which  $E_{+}$  can depend. By insisting that  $h_{11} = h_{22}$  and  $h_{12} = 0$ , the dimension of the space in which E<sub>+</sub> can intersect is reduced to 3N - 7 or 3N - 8 (for two states of the same symmetry for a nonlinear molecule). Hence, states of the same symmetry can cross, though they cross on a surface whose dimension is two less than that of the potential energy surfaces on which the molecule is moving. As a result, the molecule does not frequently encounter such crossing geometry, so the fact that the surfaces may actually cross at special points is not particularly important. The essential point is that when surfaces approach one another closely (e.g., in the neighborhoods of crossings), transitions are likely to occur. (The rates of these transitions are discussed in Chapter 6.) The extension of the above analysis to intersections among more than two surfaces is nontrivial and has been given by Alden Mead (1979).

In summary, the potential energy surfaces upon which chemists usually

' and photochemical



#### Figure 1-1

Potential energy surface of  $X^{1}\Sigma$  ground-state HCN as a function of the location of the H atom for fixed CN bond length. The minimum on this surface is located at the linear ( $\theta = 180^{\circ}$ ) geometry with the H atom bonded to the C atom.

reactions can be thought of as solutions to the Born-Oppenheimer version of the *electronic* Schrödinger equation (equation 3). The dependence of these electronic energy levels  $\{E_k\}$  on the internal coordinates of the molecule is what generates the potential surfaces that are depicted in many texts (for example, see Eyring, Walter, and Kimball, 1944; Pearson, 1976). This concept is illustrated in Figures 1-1 and 1-2 by contour graphs of the potential energy surfaces of the ground  $(X^1\Sigma)$  and  $n\pi^*$  excited (C<sup>1</sup>A') states of HCN as functions



#### Figure 1-2

Potential energy surface of the C<sup>1</sup>A' state of HCN as a function of the location of the H atom for fixed CN bond length. Note the potential well at an HCN angle near 140° and the barrier at 180°. Dashed contours are lower in energy than the solid contours.