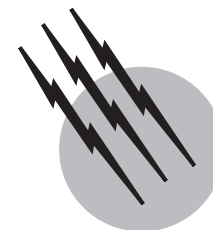


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# Potential Energy Surfaces

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## GLOSSARY

**Adiabatic representation** Representation in which the electronic wave functions are calculated for fixed (i.e., nonmoving) nuclei.

**Avoided intersection** Case in which two potential energy surfaces come together but do not intersect.

**Conical intersection** Case in which two potential energy surfaces intersect such that their separation decreases to zero linearly in the relevant nuclear coordinates.

**Diabatic representation** Representation in which the electronic wave function is not adiabatic.

**Dunham expansion** Taylor series expansion of a potential energy curve in the vicinity of its minimum.

**Electron affinity** Binding energy of an electron to a neutral atom or molecule.

**Equilibrium configuration** Geometry of a molecule's nuclear framework corresponding to the minimum adiabatic energy.

**Force field** The gradient of the potential energy surface.

**Glancing intersection** Case in which two potential energy surfaces intersect such that their separation decreases to zero quadratically in the relevant nuclear coordinates.

**Ionization energy** Energy required to remove an electron from an atom or molecule.

**A POTENTIAL ENERGY SURFACE** is an effective potential function for molecular vibrational motion or atomic and molecular collisions as a function of internuclear coordinates. The concept of a potential energy surface is basic to the quantum mechanical and semiclassical description of molecular energy states and dynamical processes. It arises from the great mass disparity between nuclei and electrons (a factor of 1838 or more) and may be understood by considering electronic motions to be much faster than nuclear motions. (When we say nuclear motions and nuclear degrees of freedom in this article, we refer to motions of the nuclei considered as wholes, i.e., to atomic motions.) This difference in timescales leads to the so-called electronic adiabatic approximation and to

electronic adiabatic potential energy surfaces. Under some circumstances, however, it is convenient to use more general definitions; this results in potential energy surfaces variously known as diabatic or nonadiabatic, the latter adjective being a useful double negative (it is convenient to use this term because, except for a few small terms, adiabatic surfaces may be defined uniquely but in general diabatic surfaces are not; nonadiabatic has the useful connotation then of “anything except the adiabatic”). The concept of potential energy surfaces may be generalized to systems in liquids, in which case one obtains potentials of mean force.

## I. INTRODUCTION

The separation of electronic and nuclear motions according to time scales and the consequent introduction of an effective potential energy surface for nuclear motion was first considered by Born and Oppenheimer. Although their method is seldom used in modern work, the modern equivalents are still commonly called Born–Oppenheimer approximations and Born–Oppenheimer potential energy surfaces. The modern form of the derivation, which is summarized below, dates to a later paper by Born and to work by Born and Huang. Occasionally the phrases Born–Oppenheimer and Born–Huang are used to specify whether certain small terms are included in the potential energy surfaces, although, as mentioned above, it is more common to refer to any adiabatic surfaces as Born–Oppenheimer surfaces.

A potential energy surface is an effective potential energy function for the relevant nuclear degrees of freedom. The latter are usually defined as all nuclear degrees of freedom minus three overall translations and two or three rotations of the nuclear subsystem. If an atom has  $N$  nuclei, it is common to consider the potential energy as a function of  $3N - 5$  coordinates for  $N = 2$  (since two nuclei always lie on a line and therefore, when considered as point masses, have only two rotational degrees of freedom) and  $3N - 6$  coordinates otherwise. Thus for  $N = 2$  we actually have a potential energy curve (i.e., a function of one variable), whereas for  $N \geq 3$  we have a potential energy hypersurface (i.e., a function of three or more variables). A potential energy surface would strictly speaking denote the potential energy as a function of two coordinates in a two-dimensional cut through the  $(3N - 6)$ -dimensional internal-coordinate space. In this article, however, we follow the very common language by which any potential energy hypersurface or potential energy function is referred to as a surface.

## II. QUANTUM MECHANICAL BASIS FOR ADIABATIC POTENTIAL ENERGY SURFACES

The Schrödinger equation for a system of  $N$  nuclei and  $n$  electrons is

$$(H - E)\Psi(\mathbf{r}, \mathbf{R}) = 0, \quad (1)$$

where  $H$  is the Hamiltonian or energy operator of the molecule:

$$H = -\frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R}) + H_{\text{rel}}(\mathbf{r}, \mathbf{R}). \quad (2)$$

In these equations,  $\hbar$  is Planck’s constant divided by  $2\pi$ , and  $\mathbf{R}$  denotes a  $3N$ -dimensional vector of scaled nuclear coordinates:

$$R_1 = \left(\frac{M_1}{M}\right)^{1/2} X_1, \quad (3a)$$

$$R_2 = \left(\frac{M_1}{M}\right)^{1/2} Y_1, \quad (3b)$$

⋮

$$R_{3N} = \left(\frac{M_N}{M}\right)^{1/2} Z_N, \quad (3c)$$

where  $M_j$ ,  $X_j$ ,  $Y_j$ , and  $Z_j$  are the mass and Cartesian coordinates of the nucleus  $j$ ,  $M$  is any of the nuclear masses or a convenient reduced nuclear mass,  $m$  is the electronic mass,  $\mathbf{r}$  is a  $3n$ -dimensional vector of electronic Cartesian coordinates  $\{x_k, y_k, z_k\}_{k=1}^n$ :

$$r_1 = x_1, \quad (4a)$$

$$r_2 = y_1, \quad (4b)$$

⋮

$$r_{3n} = z_n, \quad (4c)$$

$V(\mathbf{r}, \mathbf{R})$  is the sum of all coulomb forces between the particles,  $H_{\text{rel}}(\mathbf{r}, \mathbf{R})$  is the energy operator for relativistic effects including mass-velocity and spin–orbit coupling,  $E$  is the total energy, and  $\psi(\mathbf{r}, \mathbf{R})$  is the wave function. Notice that the first two terms in Eq. (1) represent the nonrelativistic kinetic energy of the nuclei and the electrons. Usually the change in  $\psi(\mathbf{r}, \mathbf{R})$  is about the same order of magnitude when we move a nucleus a small amount as when we move an electron the same small amount. When this is the case,  $\nabla_{\mathbf{R}}^2 \psi(\mathbf{r}, \mathbf{R})/M$  is smaller than  $\nabla_{\mathbf{r}}^2 \psi(\mathbf{r}, \mathbf{R})/m$  by a factor of order  $m/M$ , which is less than about  $10^{-3}$ ; thus the first term in Eq. (2) may be neglected to a first approximation.

The physical interpretation of this is that because of their larger masses, the nuclei move so slowly compared

with the electrons that the dependence of the wave function on electronic coordinates is essentially the same as if the nuclei were completely stationary (i.e., as if their mass were infinite so that their kinetic energy was zero). Then Eq. (1) becomes

$$\left[ -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R}) + H_{\text{rel}}(\mathbf{r}, \mathbf{R}) - U_{\alpha}(\mathbf{R}) \right] \times \psi_{\alpha}(\mathbf{r}; \mathbf{R}) = 0, \quad (5)$$

where  $U_{\alpha}(\mathbf{R})$  and  $\psi_{\alpha}(\mathbf{r}; \mathbf{R})$  denote the eigenvalue and eigenfunction, respectively, with index  $\alpha$ . Notice that both of these depend parametrically on the nuclear positions  $\mathbf{R}$  and also that the  $\psi_{\alpha}(\mathbf{r}, \mathbf{R})$  form a complete set of functions of  $\mathbf{r}$  for any particular value of  $\mathbf{R}$ . In general the spectrum  $\{U_{\alpha}(\mathbf{R})\}$  contains a continuous part as well as a discrete part, but the discrete part is the important part for the concept of potential energy surfaces. We shall therefore use only a discrete index  $\alpha$ . This is adequate for almost all practical work since the continuous part is usually neglected in calculations. For a more rigorous derivation, however, all sums over discrete  $\alpha$  in the equations below must be replaced by a sum and an integral.

To obtain the complete system wave function we choose a trial function

$$\psi(\mathbf{r}, \mathbf{R}) = \sum_{\alpha} \psi_{\alpha}(\mathbf{r}; \mathbf{R}) \chi_{\alpha}(\mathbf{R}). \quad (6)$$

Since the  $\{\psi_{\alpha}(\mathbf{r}; \mathbf{R})\}$  are complete, this trial function yields the exact  $\psi(\mathbf{r}, \mathbf{R})$  if we retain the complete set and solve for  $\{\chi_{\alpha}(\mathbf{R})\}$  by the variation method. The best  $\{\chi_{\alpha}(\mathbf{R})\}$  by this method satisfy the equation

$$\int d\mathbf{r} \psi_{\beta}^*(\mathbf{r}; \mathbf{R}) (H - E) \sum_{\alpha} \psi_{\alpha}(\mathbf{r}; \mathbf{R}) \chi_{\alpha}(\mathbf{R}) = 0, \quad \beta = 1, 2, \dots, \infty. \quad (7)$$

If we carry out the indicated operations, using Eq. (5) and the orthogonality of the  $\{\psi_{\alpha}(\mathbf{r}; \mathbf{R})\}$  in  $\mathbf{r}$  at fixed  $\mathbf{R}$ , Eqs. (7) become

$$\begin{aligned} -\frac{\hbar^2}{2M} \left[ \nabla_{\mathbf{R}}^2 \chi_{\alpha}(\mathbf{R}) + 2 \sum_{\beta} \mathbf{F}_{\alpha\beta}(\mathbf{R}) \cdot \nabla_{\mathbf{R}} \chi_{\beta}(\mathbf{R}) \right. \\ \left. + \sum_{\beta} G_{\alpha\beta}(\mathbf{R}) \chi_{\alpha\beta}(\mathbf{R}) \right] + [U_{\alpha}(\mathbf{R}) - E] \chi_{\alpha}(\mathbf{R}) = 0, \\ \alpha = 1, 2, \dots, \infty, \quad (8) \end{aligned}$$

where

$$\mathbf{F}_{\alpha\beta}(\mathbf{R}) = \int d\mathbf{r} \psi_{\alpha}^*(\mathbf{r}; \mathbf{R}) \nabla_{\mathbf{R}} \psi_{\beta}(\mathbf{r}; \mathbf{R}) \quad (9)$$

and

$$\mathbf{G}_{\alpha\beta}(\mathbf{R}) = \int d\mathbf{r} \psi_{\alpha}^*(\mathbf{r}; \mathbf{R}) \nabla_{\mathbf{R}}^2 \psi_{\beta}(\mathbf{r}; \mathbf{R}). \quad (10)$$

By the same argument given above for the variation of  $\psi(\mathbf{r}, \mathbf{R})$  with respect to  $\mathbf{r}$  and  $\mathbf{R}$ , we expect that the terms containing  $\mathbf{F}_{\alpha\beta}(\mathbf{R})$  and  $G_{\alpha\beta}(\mathbf{R})$  are usually much smaller than the term containing  $U_{\alpha}(\mathbf{R})$ . When this is so, we may neglect the small terms, and the set of coupled Eqs. (8) simplifies to a separate uncoupled equation for each  $\chi_{\alpha}(\mathbf{R})$ , namely,

$$\left[ -\frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2 + U_{\alpha}(\mathbf{R}) - E \right] \chi_{\alpha}(\mathbf{R}) = 0. \quad (11)$$

This has the form

$$(H_{\text{nuc}} - E) \chi_{\alpha}(\mathbf{R}) = 0, \quad (12)$$

where  $H_{\text{nuc}}$  is an effective Hamiltonian for nuclear motion given by

$$H_{\text{nuc}} = -\frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2 + U_{\alpha}(\mathbf{R}). \quad (13)$$

Since a Hamiltonian is usually the sum of a kinetic energy operator and a potential energy operator, we may interpret  $U_{\alpha}(\mathbf{R})$  as an effective potential for nuclear motion. In fact,  $U_{\alpha}(\mathbf{R})$  is the potential energy surface that we sought to derive. Recalling the origin of  $U_{\alpha}(\mathbf{R})$ , we see that it represents the total energy of the electrons, both kinetic and potential, plus all the rest of the potential energy, when the electrons are in state  $\alpha$ . Alternatively, it represents the entire (coulombic plus relativistic) potential energy of all particles plus the electrons' kinetic energy. When the equations for the  $\chi_{\alpha}(\mathbf{R})$  decouple, as in Eq. (12), the electronic state is preserved during the nuclear motion. The resulting quantized energy requirement of the electrons plus the rest of the potential energy (given in the absence of relativistic effects by the nuclear–nuclear coulombic interaction energy) together constitute an effective potential for nuclear motion.

When nuclear motion can be approximated by classical mechanics (which is often reasonable, especially for atoms heavier than hydrogen), Eqs. (12) and (13) are replaced by

$$M\ddot{\mathbf{R}} = -\nabla_{\mathbf{R}} U_{\alpha}(\mathbf{R}), \quad (14)$$

where  $\ddot{\mathbf{R}}$  is the nuclear acceleration, and the right-hand side is the force on the nuclei. Since  $U_{\alpha}(\mathbf{R})$  generates the force function, it is sometimes called the force field.

Inclusion of the spin–orbit and other relativistic terms in Eq. (5), as we have done, is, strictly speaking, the most correct approach. This yields, as we have seen, a set of nuclear wave functions  $\chi_{\alpha}(\mathbf{R})$  whose uncoupled motion is governed by the potentials  $U_{\alpha}(\mathbf{R})$  and which are coupled only by the nuclear-derivative terms  $\mathbf{F}_{\alpha\beta}(\mathbf{R})$  and  $G_{\alpha\beta}(\mathbf{R})$ . In practice, though,  $H_{\text{rel}}(\mathbf{R})$  is difficult to treat on an equal footing with the coulombic terms in the Hamiltonian. Therefore one sometimes works with

nonrelativistic adiabatic potential surfaces, although the adjective *nonrelativistic* is seldom stated explicitly. In this approximation one temporarily neglects  $H_{\text{rel}}(\mathbf{r}, \mathbf{R})$  to solve Eq. (5). This yields a new set of nuclear wave functions  $\chi_\alpha(\mathbf{R})$  and  $U_\alpha(\mathbf{r}, \mathbf{R})$  that are easier to work with, but the effect of  $H_{\text{rel}}(\mathbf{r}, \mathbf{R})$  must be included later. The matrix elements

$$H_{\text{rel},\alpha\beta}(\mathbf{R}) = \int d\mathbf{r} \psi_\alpha^*(\mathbf{r}; \mathbf{R}) H_{\text{rel}}(\mathbf{r}, \mathbf{R}) \psi_\beta(\mathbf{r}; \mathbf{R}) \quad (15)$$

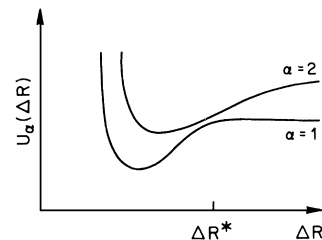
provide both a perturbative correction to the nonrelativistic potential energy surfaces, for  $\alpha = \beta$ , and an additional coupling mechanism that must be considered along with  $\mathbf{F}_{\alpha\beta}(\mathbf{R})$  and  $U_{\alpha\beta}(\mathbf{R})$  for  $\alpha \neq \beta$ . In the rest of this article we restrict our attention to the nonrelativistic approximation, and we assume that  $H_{\text{rel}}(\mathbf{r}, \mathbf{R})$  has been neglected in solving Eq. (5).

### III. TOPOLOGY OF ADIABATIC POTENTIAL ENERGY SURFACES

As shown in Eq. (5), an adiabatic potential energy surface is an eigenvalue of a Hermitian operator, that is, one that has only real eigenvalues. In most cases these eigenvalues are nondegenerate. At some geometries  $\mathbf{R}$ , however, two or more eigenvalues may be equal, which is called a degeneracy. Such degeneracies may be mandated by symmetry or may be accidental. Points where two or more eigenvalues are equal are particularly interesting, and we may categorize some features of the potential energy surfaces in the neighborhoods of these points on the basis of symmetry.

The nuclear configuration  $\mathbf{R}$ , which appears as a parameter in the eigenvalue Eq. (5), may be classified by a symmetry point group, for example,  $D_{\infty h}$  for a homonuclear diatomic molecule or another symmetric linear molecule,  $C_{\infty v}$  for a heteronuclear diatomic molecule or other non-symmetric linear molecule,  $T_d$  for a tetrahedral molecule,  $C_{2v}$  for a symmetric nonlinear triatomic molecule, and  $C_s$  for a planar molecule. Since the operations of such a group commute with  $-(\hbar^2/2M)\nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R})$ , the eigenfunctions  $\psi_\alpha(\mathbf{r}, \mathbf{R})$  of this operator can be taken to transform as irreducible representations of the group. We may thus classify both the eigenfunctions  $\psi_\alpha(\mathbf{r}, \mathbf{R})$  and eigenvalues  $U_\alpha(\mathbf{R})$  by these irreducible representations, e.g.,  $\Sigma_g^+$ ,  $\Pi_u$ , or  $\Delta_g$  for  $D_{\infty h}$  or  $A_1$  or  $B_2$  for  $C_{2v}$ .

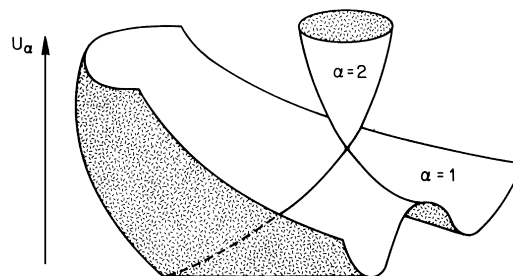
First consider the case of two nuclei. As already mentioned, the potential energy surfaces in this case are really curves; they depend on only one scalar variable, the internuclear distance, which we may call  $\Delta R$ . One can show, on general grounds, that for a system with an even number of electrons, two  $U_\alpha(\Delta R)$  may be accidentally equal



**FIGURE 1** An avoided crossing for a diatomic molecule.  $U_a$  is the potential energy for electronic state  $a$ ,  $\Delta R$  the internuclear distance, and  $\Delta R^*$  the distance corresponding to an avoided crossing.

at isolated values of  $\Delta R$  if they correspond to different symmetry but not if they correspond to the same symmetry. When two  $U_\alpha(\Delta R)$  are equal, that is called a curve crossing. Sometimes two  $U_\alpha(\Delta R)$  approach very closely as if they are about to cross but then avoid crossing. This is called an avoided crossing. An example is shown in Fig. 1. When the system has an odd number of electrons and exists in a magnetic-free region, the possibilities are the same except that all  $U_\alpha(\Delta R)$  occur in degenerate pairs. Imposition of a magnetic field removes the degeneracy.

Now consider the case of  $N \geq 3$  for which the potential energy surfaces depend on three or more variables. Here we also find potential surface intersections of states belonging to different symmetries and avoided intersections of states belonging to the same symmetry, but there is also a third possibility, namely, intersections even of potential energy surfaces belonging to the same symmetry. Such intersections in general occur in subspaces of dimension  $3N - 8$  or lower. If we consider a subset of two degrees of freedom in which the intersection occurs at a single point, the shape of the surfaces in the vicinity of the intersection is as shown in Fig. 2, that is, the two surfaces form a double cone. Such intersections are called conical intersections. Another shape of intersection may occur at linear geometries of polyatomic molecules. In this case, the two surfaces may have zero slope at the point of intersection. Such intersections are called glancing rather than conical.



**FIGURE 2** Portions of two potential energy surfaces exhibiting a conical intersection.  $U_a$  is the potential energy for electronic state  $a$ .

In general, for systems of three or more nuclei, some potential energy surfaces that intersect when one neglects spin-orbit coupling avoid intersecting when one includes it.

#### IV. BREAKDOWN OF THE ADIABATIC APPROXIMATION

We are now in a position to understand the limitations of the adiabatic potential energy surface concept. First, however, we should understand the physical origin of avoided crossings and avoided intersections. We begin by considering the diatomic molecule NaCl, and we let  $\Delta R$  denote the distance between the nuclei. At  $\Delta R = \infty$ , the energy of two neutral atoms is lower than the energy of a  $\text{Na}^+$  ion and a  $\text{Cl}^-$  ion by the difference  $\Delta E$  of the ionization potential of Na and the electron affinity of  $\text{Cl}^-$ . As  $\Delta R$  is decreased, however, the energy of the ionic state decreases rapidly because of the long-range coulomb attraction, which may be represented by  $-e^2/\Delta R$  where  $e$  is the electronic charge, while the energy of the neutral state stays approximately constant until much shorter distances where the covalent interaction becomes appreciable. Thus at some distance  $\Delta R^*$  given approximately by

$$\Delta E \cong \frac{e^2}{\Delta R^*} \quad (16)$$

the hypothetical purely ionic state and the hypothetical purely covalent state would have the same energy. Actually though, at this  $\Delta R$  the corresponding eigenfunctions of Eq. (5) have mixed character, partly covalent and partly ionic, with about 50% partial ionic character. Since both states have  $^1\Sigma_g^+$  character, their eigenvalues are different. We call the energies of the hypothetical states with pure valence characteristics  $U_1^d(\Delta R)$  and  $U_2^d(\Delta R)$ , where  $d$  denotes diabatic (or nonadiabatic). Although  $U_1^d(\Delta R)$  and  $U_2^d(\Delta R)$  cross, the adiabatic curves  $U_1(\Delta R)$  and  $U_2(\Delta R)$  avoid crossing, having the shapes shown in Fig. 1. For this case  $\alpha = 1$  corresponds to a covalent state to the right of  $\Delta R^*$  but to an ionic state to the left of  $\Delta R^*$  and vice versa for  $\alpha = 2$ . Now recall the argument given above for neglecting  $\mathbf{F}_{12}(\mathbf{R})$  and  $G_{12}(\mathbf{R})$ . At  $\Delta R = \Delta R^*$ , the wave function is changing character very rapidly as a function of  $\Delta R$ , and the action of  $\nabla_{\mathbf{R}}$  on  $\psi(\mathbf{r}, \mathbf{R})$  is unusually large; this means that  $\mathbf{F}_{12}(\Delta R)$  and  $G_{12}(\Delta R)$  need not be negligible. In such a case, the dynamics governed by the nuclear-motion wave functions  $\chi_1(R)$  and  $\chi_2(R)$  do not decouple into independent motions governed by effective potentials (i.e., the adiabatic potential energy surface concept breaks down). Although we have given the argument for a particular diatomic molecule, the effect is general, and the

adiabatic approximation is expected to break down in the vicinity of any avoided crossing or avoided intersection, and also at actual intersections for which the symmetry of the two states is the same at the intersection.

There are other circumstances under which the adiabatic approximation may break down. We have considered the case where  $\psi(\mathbf{r}, \mathbf{R})$  varies rapidly with  $\mathbf{R}$  because of the factor  $\psi_{\alpha}(\mathbf{r}; \mathbf{R})$ . A second case where the term containing  $\mathbf{F}_{\alpha\beta}(\mathbf{R})$  in Eq. (8) may be significant occurs when  $\chi_{\alpha}(\mathbf{R})$  varies unusually rapidly, for instance, in highenergy collisions of  $\text{Na}^+$  with  $\text{Cl}^-$ . When the nuclear speed is large,  $\chi_{\alpha}(\mathbf{R})$  must vary significantly on the scale of a very small de Broglie wavelength.

We may summarize the two cases in a simple but approximate way as follows: When the nuclear kinetic energy is much smaller than the spacings between the adiabatic electronic energy surfaces  $U_{\alpha}(\mathbf{R})$ , these surfaces serve as potential energy surfaces for nuclear motion. When the nuclear kinetic energy is comparable to or larger than the spacings between the  $U_{\alpha}(\mathbf{R})$ , the adiabatic approximation may, and often does, break down.

The adiabatic potential energy surfaces need not be abandoned completely when the adiabatic approximation breaks down, especially if the region of breakdown is fairly localized, as it often is when the breakdown is due to an avoided or conical intersection. If the nonadiabatic behavior is localized to a small region, we often employ the model of surface hopping. In this model the nuclear motion is assumed to be governed by an adiabatic potential energy surface until a nonadiabatic region is reached. In such a region there is a nonzero quantum mechanical probability that the system ‘‘hops’’ to another surface. Based on this probability one portion of the quantum mechanical probability density exits the nonadiabatic region in one of the adiabatic electronic states, and the other portion exits in the other one or more coupled adiabatic electronic states. After this the nuclear motions again proceed independently as governed by single potential energy surfaces until another nonadiabatic region is reached. Although this model neglects certain coherency effects that may be important for quantitative work, it is often useful for qualitative discussions and semiquantitative calculations.

Another concept often invoked for qualitative discussions and for calculations when the adiabatic approximation breaks down is that of diabatic potential energy surfaces. There are several nonequivalent ways of defining such surfaces, each of which may be useful under some circumstances. The simplest way is that already illustrated above in conjunction with the NaCl example: namely, a diabatic state is the effective potential energy function for nuclear motion when the electronic state is artificially constrained to a state of prespecified pure valency.

A second way to define diabatic electronic states and potential energy surfaces is more mathematical. Notice that the valency-character prescription leads to states coupled by the operator

$$H_{\text{el}} = -\frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R}) + H_{\text{rel}}(\mathbf{r}, \mathbf{R}) \quad (17)$$

and also by  $-(\hbar^2/2M)\nabla_{\mathbf{R}}^2$ . From the point of view of the nuclear motion, the former is sometimes called potential coupling (since it involves only multiplicative operators in the nuclear coordinates), and the latter is called derivative coupling. Since electronically adiabatic states have derivative coupling but no electronic coupling, a natural question is whether useful diabatic states can be defined to have potential coupling but not derivative coupling. Unfortunately, this leads to states that are completely independent of  $\mathbf{R}$  and are not useful. It is possible, however, to make one component (in one or another coordinate system) of the vector coupling operator  $\mathbf{F}_{\alpha\beta}(\mathbf{R})$  vanish for all  $\alpha, \beta$ . Furthermore, if  $\mathbf{F}_{\alpha\beta}(\mathbf{R})$  is approximated as the gradient of a scalar (which can be a good approximation when nonadiabatic effects are dominated by a narrowly avoided intersection), then it is possible to make all components of  $\mathbf{F}_{\alpha\beta}(\mathbf{R})$  vanish for all  $\alpha, \beta$ . Both of these prescriptions are sometimes employed to obtain diabatic states. Consider, for example, the case where  $\mathbf{F}_{\alpha\beta}(\mathbf{R})$  is the gradient of a scalar for all  $\mathbf{R}$ ; then it has zero curl. We define diabatic electronic states by

$$\phi_{\alpha}^{\text{d}}(\mathbf{r}; \mathbf{R}) = \sum_{\beta} \phi_{\beta}(\mathbf{r}; \mathbf{R}) T_{\beta\alpha}(\mathbf{R}). \quad (18)$$

The states  $\{\phi_{\alpha}^{\text{d}}(\mathbf{r}; \mathbf{R})\chi_{\alpha}^{\text{d}}(\mathbf{R})\}$  will be uncoupled by nuclear derivative operators if we choose  $T_{\beta\alpha}(\mathbf{R})$  for all  $\beta$  and  $\alpha$  such that

$$\nabla_{\mathbf{R}} T_{\alpha\beta}(\mathbf{R}) = \sum_{\gamma} \mathbf{F}_{\alpha\gamma}(\mathbf{R}) T_{\gamma\beta}(\mathbf{R}), \quad (19)$$

and this set of coupled partial differential equations does have a solution if  $\mathbf{F}_{\alpha\beta}(\mathbf{R})$  has zero curl. Furthermore, if the state expansion  $\alpha, \beta, \dots$  is truncated to a finite number of computationally important states, then the diabatic electronic basis is not independent of  $\mathbf{R}$ . In this way, one can define a diabatic basis by a transformation from an adiabatic one, and it spans the same space. The diabatic potential surfaces are given by

$$U_{\alpha\alpha}^{\text{d}}(\mathbf{R}) = \sum_{\gamma} |T_{\gamma\alpha}(\mathbf{R})|^2 U_{\gamma}(\mathbf{R}), \quad (20)$$

and the potential couplings are given by

$$U_{\alpha\beta}(\mathbf{R}) = \sum_{\gamma} T_{\gamma\alpha}^*(\mathbf{R}) U_{\gamma}(\mathbf{R}) T_{\gamma\beta}(\mathbf{R}). \quad (21)$$

As mentioned in Section II, the usual treatments of potential energy surfaces neglect  $H_{\text{rel}}(\mathbf{r}, \mathbf{R})$  in Eq. (5). Thus one solves

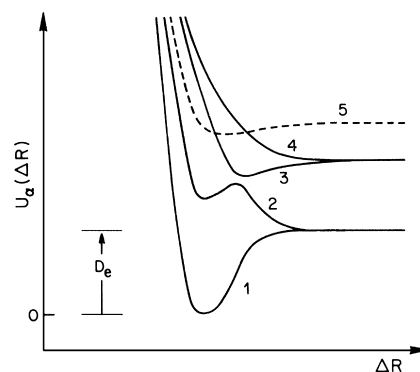
$$\left[ -\frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R}) - U_{\alpha}^{\text{n}}(\mathbf{R}) \right] \psi_{\alpha}^{\text{n}}(\mathbf{r}, \mathbf{R}) = 0, \quad (22)$$

where the superscript n denotes nonrelativistic. The true adiabatic states are coupled only by  $-(\hbar^2/2M)\nabla_{\mathbf{R}}^2$ , but these nonrelativistic adiabatic states are coupled by both this operator and  $H_{\text{rel}}(\mathbf{r}, \mathbf{R})$ . Because of the latter coupling, the nonrelativistic adiabatic electronic states  $\psi_{\alpha}^{\text{n}}(\mathbf{r}; \mathbf{R})$  and their associated potential energy curves  $U_{\alpha}^{\text{n}}(\mathbf{R})$ , which are the most widely employed states and potential energy surfaces in quantum chemistry, are actually diabatic. They are nevertheless usually called adiabatic although nonrelativistic is adiabatic is technically more appropriate.

## V. SHAPES OF POTENTIAL ENERGY SURFACES

### A. Diatomics

A schematic illustration of some typically shaped adiabatic potential energy curves for a diatomic molecule is shown in Fig. 3. All five curves shown become large and positive at small internuclear distance  $\Delta R$ . This represents a repulsive force between the nuclei and is due to internuclear repulsion and the unfavorability of overlapping the atomic charge clouds of the two different centers. All five curves tend to constants at large  $\Delta R$ . This is because the atomic interaction energy eventually decreases to zero as the distance between the atoms is increased. The constant spacings between the curves at large  $\Delta R$  are equal to the atomic excitation energies. Curves 1 and 2 are effective potentials for the interaction of ground-state atoms, and curves 3–5 represent effective potentials for the case where at least one of the atoms is excited. The figure shows an avoided crossing between curves 2 and 3 and



**FIGURE 3** Typical potential energy curves for a diatomic molecule ordinarily thought of as bound.  $U_{\alpha}$  and  $\Delta R$  are as in Fig. 1;  $D_e$  is the equilibrium bond energy of the ground state. Curves 1–5 are discussed in the text.

true crossings of curves 3 and 4 by curve 5. Curves with deep enough minima, such as 1 and 3, may possess bound states of nuclear motion. Classically, a pair of nuclei whose motion is governed by one of these curves could show simple, almost-harmonic motion in the vicinity of the minimum of the curve. Quantally, there could be bound vibrational states localized in these regions of  $\Delta R$ . Curve 1 has the typical shape for the ground electronic state of a stable molecule such as  $H_2$ ,  $N_2$ , or  $HCl$ . Such a curve is often represented in the vicinity of the minimum by a quadratic potential:

$$U_\alpha(\Delta R) \cong \frac{1}{2}k(\Delta R - R_e)^2, \quad (23)$$

where  $k$  is the force constant (actually the quadratic force constant) and  $R_e$  the equilibrium internuclear distance. An analytic representation valid over a wider range of  $\Delta R$  is given by

$$U_\alpha(\Delta R) \cong \frac{1}{2}k_{11}(\Delta R - R_e)^2 + \frac{1}{2}k_{111}(\Delta R - R_e)^3 + \frac{1}{2}k_{1111}(\Delta R - R_e)^4 + \dots, \quad (24)$$

where  $k$  has been renamed  $k_{11}$ , and  $k_{111}$  and  $k_{1111}$  are anharmonic (cubic and quartic) force constants. Sometimes the constant coefficient of  $(\Delta R - R_e)^j$  is written  $1/j!$  instead of  $\frac{1}{2}$  so care must be exercised when using anharmonic force constants. Equation (24) is called a Dunham expansion. An approximate representation of a potential curve like curve 1 in Fig. 3 that gives its approximate shape over the full range of  $\Delta R$  is

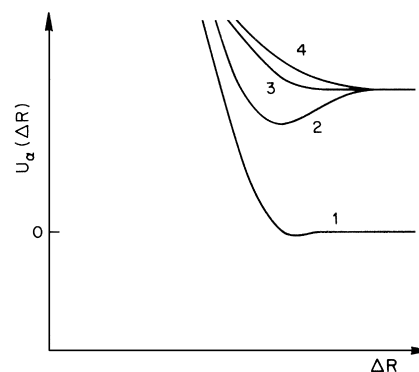
$$U_\alpha(\Delta R) = D_e\{1 - \exp[-\alpha(\Delta R - R_e)]\}^2. \quad (25)$$

This is called a Morse curve,  $D_e$  the equilibrium dissociation energy, and  $\alpha$  the Morse range parameter. More complicated analytic forms with more parameters are also used.

Information about the various parameters ( $R_e$ ,  $k_{11}$ ,  $k_{111}$ ,  $\dots$ ,  $D_e$ , and  $\alpha$ ) comes primarily from spectroscopy, scattering or kinetics experiments, and quantum mechanical electronic structure calculations. These are also the sources for information about potential energy surfaces of systems with three or more atoms.

Figure 4 shows, to about the same scale as Fig. 3, some typically shaped potential curves for a diatomic system usually thought of as unbound (e.g.,  $He_2$ ,  $HeNe$ , or  $ArH$ ). Notice that the lowest potential energy curve has only a very small minimum at large  $\Delta R$ . When this minimum is important for the problem at hand, such a potential energy curve is often represented by a Lennard–Jones 12–6 potential:

$$U_\alpha(\Delta R) = 4\varepsilon \left[ \left( \frac{\sigma}{\Delta R} \right)^{12} - \left( \frac{\sigma}{\Delta R} \right)^6 \right], \quad (26)$$



**FIGURE 4** Typical potential energy curves for a pair of atoms ordinarily thought of as unbound.  $U_\alpha$  and  $\Delta R$  are as in Fig. 1. See text for discussion of the curves.

where  $\varepsilon$  is the well depth and  $\sigma$  the collision diameter. Notice that the minimum of  $U_\alpha(R)$  occurs at  $\Delta R = R_m$  where

$$R_m = 2^{1/6}\sigma \quad (27)$$

and that

$$U_\alpha(\Delta R = R_m) = -\varepsilon. \quad (28)$$

When the minimum of a predominantly repulsive potential curve is considered negligible, it may be represented by a so-called anti-Morse curve:

$$U_\alpha(\Delta R) = D^{AM}\{\exp[-2\beta(\Delta R - R^{AM})] + 2\exp[-\beta(\Delta R - R^{AM})]\} + C^{AM}, \quad (29)$$

where  $D^{AM}$ ,  $\beta$ ,  $R^{AM}$ , and  $C^{AM}$  are constants, or even by the simpler

$$U_\alpha(\Delta R) = \left( \frac{\beta}{\Delta R} \right) \exp(-\alpha\Delta R). \quad (30)$$

Equation (29) or (30) could be applied to curve 4 of Fig. 3, to curve 1, 3, or 4, of Fig. 4, or even to curve 2 of Fig. 3, for which it might be useful in the region to the right of the avoided crossing and to the left of the shallow, large- $\Delta R$  minimum.

Notice that the zero of energy is arbitrary for potential energy surfaces as long as it is chosen consistently throughout a given calculation. In Fig. 3 we placed the zero of energy at the bottom of the lowest potential curve. In Fig. 4 we placed it at the energy of two separated ground-state atoms.

## B. Larger Molecules

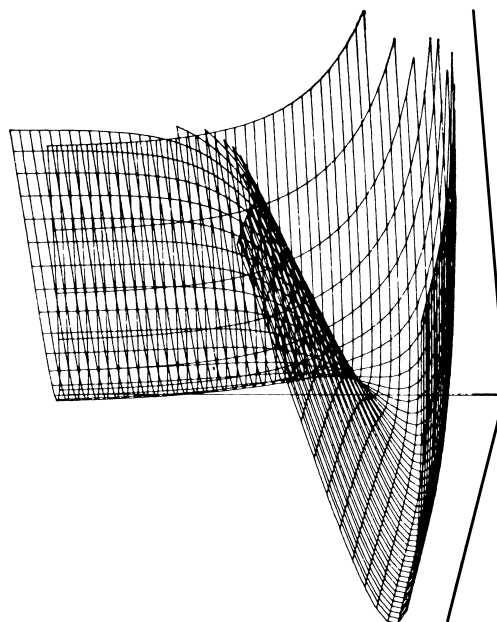
Potential energy surfaces for systems with three or more atoms are harder to illustrate because they depend on three or more internal coordinates. Analytic representations are also more complicated than for diatomics.

Potential energy surfaces may be roughly classified into those with deep enough minima to support one or more strongly bound vibrational states and those without such minima. We shall call the former attractive surfaces because of the role played by the attractive forces between the atoms in creating the minimum. The latter will be called repulsive surfaces. Because spacings between potential energy curves are usually much larger than thermal energies, most molecular motions under ordinary conditions are usually governed by the lowest energy potential surface. Thus molecules that usually exist as bound, stable entities (e.g.,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , or  $\text{CH}_4$ ) have attractive surfaces in their ground (i.e., lowest energy) electronic states, whereas molecules usually observed only as transient species during collisions (e.g.,  $\text{FH}_2$  which exists during  $\text{F} + \text{H}_2$  or  $\text{H} + \text{HF}$  collisions or  $\text{NeH}_2\text{O}$ , which exists during  $\text{Ne} + \text{H}_2\text{O}$  collisions) have repulsive surfaces. Systems like  $\text{Ne}_2$  or  $\text{NeH}_2\text{O}$  may exist as stable but very weakly bound (and thus easily and usually dissociated) species because of shallow potential wells in predominantly repulsive potential energy surfaces. Such weakly bound species are called van der Waals molecules. Systems with attractive surfaces in their ground electronic states may have repulsive surfaces in excited (i.e., higher-energy) electronic states, and vice versa. Examples of van der Waals wells and repulsive excited states for the easily illustrated special case of diatomic molecules may be seen in Figs. 3 and 4.

The most well understood region of attractive potential energy surfaces is usually the region near the minimum. One usually describes the potential energy surface in such a vicinity by a Taylor's series about the minimum:

$$\begin{aligned}
 U_\alpha(\mathbf{R}) = & U_e + \frac{1}{2} \sum_i \sum_j k_{ij} q_i q_j \\
 & + \frac{1}{2} \sum_i \sum_j \sum_k k_{ijk} q_i q_j q_k \\
 & + \frac{1}{2} \sum_i \sum_j \sum_k \sum_l k_{ijkl} q_i q_j q_k q_l + \dots,
 \end{aligned}
 \tag{31}$$

where  $U_e$ ,  $k_{ij}$ ,  $k_{ijk}$ ,  $\dots$  are constants, and the  $\{q_j\}$  are suitable internal coordinates defined to vanish at the location of the minimum. As written, Eq. (31) contains no terms linear in the  $\{q_j\}$ , but if these are not related to Cartesian coordinates by a linear transformation, it may be necessary to include linear terms. Equation (31) is called an anharmonic force field. If the coordinates are linear combinations of Cartesians and terms beyond the quadratic are neglected, it becomes a harmonic force field. In the harmonic approximation it is always possible to define the  $\{q_j\}$  in such a way that the cross terms vanish (i.e.,  $k_{ij} = 0$



**FIGURE 5** Perspective view of potential energy surface for collinear  $\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$ . The vertical axis is potential energy, and axes in the horizontal plane are nearest-neighbor distances.

if  $i \neq j$ ). If this is done and cross terms vanish in the kinetic energy operator as well, Eq. (31) is called a normal-mode expansion.

In the vicinity of the minimum of the surface, a two-dimensional cut through an attractive potential energy surface has the shape of a distorted paraboloid of revolution.

Figure 5 shows a perspective view of a cut through a potential energy surface for a chemical reaction; in particular it is based on an approximate surface for the reaction  $\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$ . To represent the potential as a function of two internal coordinates, the three atoms are restricted for this figure to lie on a straight line. If the hydrogens are labeled  $\text{H}_a$  and  $\text{H}_b$ , the left–right axis is the  $\text{H}_b$ -to-Cl distance with large values at the left, and the front–back axis is the  $\text{H}_a$ -to- $\text{H}_b$  distance with large values in the foreground; the third interpair distance is the sum of these two. The vertical axis is potential energy. The figure clearly shows the existence of a minimum-energy reaction path from reactants in the foreground to products at the back left. The highest energy point along the minimum-energy path is a saddle point. This point is sometimes called the transition state, and it primarily determines the threshold energy for reaction to occur. The shape of the reaction path is important for determining the reaction probability as a function of the vibrational and relative translational energy of the reactants.

Figure 6 shows the same information as in Fig. 5 but in the form of a contour map (i.e., a set of isopotential contours). The horizontal axis is the distance from Cl to



the center of mass of  $\text{H}_2$ , and the vertical axis is  $[(M_{\text{Cl}} + 2M_{\text{H}}/4M_{\text{Cl}})]^{1/2}$  times the  $\text{H}_a$ -to- $\text{H}_b$  distance. Because of the mass scaling factor, the nuclear-motion Hamiltonian, Eq. (13), in this coordinate system becomes

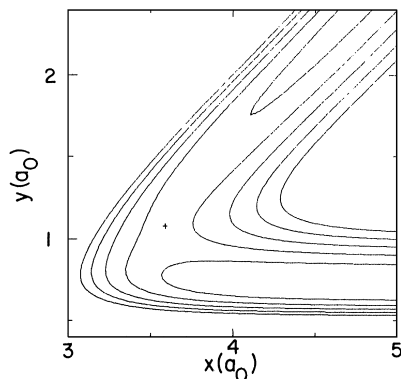
$$H_{\text{nuc}} = -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + U_{\alpha}(x, y), \quad (32)$$

where

$$\mu = \frac{2M_{\text{Cl}}M_{\text{H}}}{(M_{\text{Cl}} + 2M_{\text{H}})}. \quad (33)$$

Since the coefficient of both derivative operators is the same, this Hamiltonian is the same as that for a single particle in two dimensions under the influence of a potential function  $U_{\alpha}(x, y)$ . This analogy is very helpful in mentally visualizing the motion of a polyatomic system whose dynamics are governed by a multidimensional potential surface. In Fig. 6 the  $\text{H} + \text{HCl}$  reaction is initiated at the lower right, and products are formed when the system, having passed through or near the saddle point (denoted + in the figure), reaches the top.

For solutes in the liquid phase (e.g., an organic molecule in aqueous solution), one can obtain an effective potential



**FIGURE 6** Contour map of a potential energy surface for collinear  $\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$ .  $x$  is the distance from H to the center of mass of HCl and  $y$  the mass-scaled distance from Cl to its nearest H. Both axes are given in units of  $a_0$ , where  $1a_0 = 1 \text{ bohr} = 0.5292 \times 10^{-10} \text{ m}$ .

function of the solute coordinates by adding the free energy of solution to the gas-phase potential surface. The resulting potential function may be used in Eq. (14), and it is called a potential of mean force.

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