Born-Oppenheimer Approximation

All matter consists of nuclei and electrons that have a positive and negative charge, respectively. Electrostatic forces keep these particles together to form molecules of any size and complexity. The Schrödinger equation provides the mathematical description of the behavior of such many body systems:

$$H\Psi = E\Psi. \tag{1}$$

In this eigenvalue equation H is the system's Hamilton operator, or Hamiltonian, that returns the total energy E of the system when operating on the many-body wavefunction Ψ. As in classical mechanics, the Hamiltonian is defined as the sum of the kinetic T and potential energy V:

$$H = T + V. \tag{2}$$

From the wavefunction Ψ, all static properties of the system of interest can be derived. Dynamic information is obtained by integrating the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\Psi = H\Psi, \tag{3}$$

with $\hbar$ the Planck constant divided by 2π. Unfortunately, an exact solution exists only if there are at most two interacting particles in the system, such as for instance the hydrogen atom. Solving the equations for any larger system requires approximations.

The first approximation is to ignore relativistic effects. Only for very heavy elements, *i.e.*, that have very high nuclear charges, the inner shell electrons can move so fast that relativistic effects become important. Since biological molecules are mostly composed of first and second row elements, the electronic velocities are sufficiently low for relativistic effects to be ignored. Within this approximation, the non-relativistic Hamiltonian is given by:

$$H = T_N + T_e + U(\mathbf{r}, \mathbf{R}), \tag{4}$$

where T_e and T_N are the operators of the kinetic energy of the electrons and the nuclei, respectively, and $U(\mathbf{r}, \mathbf{R})$ is the total potential energy of the electrons and nuclei together. Since relativistic effects are ignored, no spin interactions are included in the Hamiltonian. The vector $\mathbf{r}$ denotes the set of electronic coordinates and the vector $\mathbf{R}$ stands for the nuclear coordinates.

The next approximation is to separate the motion of the electrons from that of the nuclei. This approximation provides the basis for modern quantum chemistry. The approximation rests on the mass difference between electrons and nuclei. Nuclei are much heavier than electrons, so that the latter adopt instantaneously to displacements of the former. Electrons 'see' nuclei standing still, while the nuclei move on potential energy landscapes created instantly by the faster electrons. Within this so-called 'clamped-nuclei' approximation, the electronic and nuclear wavefunctions can be treated independently.

First, the Schrödinger equation is solved for electrons moving in a framework of fixed nuclei. Thus, the nuclear kinetic energy (T_N) is dropped from the full Hamiltonian (eq. 4) to yield

$$H^e = T_e + U(\mathbf{r}, \mathbf{R}), \tag{5}$$

where the superscript e indicates the *electronic* Hamiltonian. The electronic wavefunctions are the eigenfunctions of this Hamiltonian

$$H^e\psi_i(\mathbf{r}; \mathbf{R}) = V_i(\mathbf{R})\psi_i(\mathbf{r}; \mathbf{R}), \tag{6}$$

with $\psi_i(\mathbf{r}; \mathbf{R})$ and $V_i(\mathbf{R})$ the electronic wavefunctions and their electronic energies, respectively that both depend *parametrically* on the nuclear coordinates. The wavefunctions are the adiabatic electronic states, representing the electronic ground state ($i = 0$), excited state ($i = 1$), second excited state ($i = 2$) and so on. How these wavefunctions are obtained in practical computations is the subject of modern quantum chemistry[1].

The adiabatic wavefunctions can be made *orthonormal*, *i.e.*

$$\langle \psi_i | \psi_j \rangle = \int_{-\infty}^{\infty} \psi_i(\mathbf{r}; \mathbf{R})^* \psi_j(\mathbf{r}; \mathbf{R}) d\mathbf{r} = \delta_{ij}, \tag{7}$$

where the Dirac bra-ket notation ($\langle | \rangle$) has been introduced that will be used throughout the text and where δ_{ij} is the Kronecker delta-function, which is 1 if $i = j$ and 0 otherwise.

Within the Born representation, the adiabatic electronic states provide a complete basis to expand the molecular wavefunction in:

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_j \chi_j(\mathbf{R}) \psi_j(\mathbf{r}; \mathbf{R}), \tag{8}$$

where the expansion coefficients $\chi_j(\mathbf{R})$ are the nuclear wavefunctions. Substituting the expression for the molecular wavefunction in the time-independent Schrödinger equation (eq. 1) and multiplying by the adiabatic electronic wavefunction $\psi_i^*(\mathbf{r}; \mathbf{R})$ from the left, followed by integration over the electronic coordinates $\mathbf{r}$ leads to the following set of coupled equations

$$\sum_j H_{ij}(\mathbf{R}) \chi_j(\mathbf{R}) = E(\mathbf{R}) \chi_i(\mathbf{R}), \tag{9}$$

with

$$H_{ij}(\mathbf{R}) = \langle \psi_i(\mathbf{r}; \mathbf{R}) | H | \psi_j(\mathbf{r}; \mathbf{R}) \rangle = \langle \psi_i(\mathbf{r}; \mathbf{R}) | T_N | \psi_j(\mathbf{r}; \mathbf{R}) \rangle + V_i(\mathbf{R}) \delta_{ij}. \tag{10}$$

The nuclear kinetic energy operator is defined as

$$T_N = -\sum_k \frac{\hbar^2}{2M_k} \nabla_{\mathbf{R}_k}^2, \tag{11}$$

in which M_k is the mass of nucleus k and the sum runs over all nuclei. Using this relation, equation 10 can be re-written as[2]

$$H_{ij}(\mathbf{R}) = [T_N + V_i(\mathbf{R})] \delta_{ij} - \Lambda_{ij}(\mathbf{R}). \tag{12}$$

The *non-adiabatic* operator elements $\Lambda_{ij}(\mathbf{R})$ are defined as

$$\Lambda_{ij}(\mathbf{R}) = \sum_k F_{ij}^k(\mathbf{R}) \nabla_{\mathbf{R}_k} + G_{ij}(\mathbf{R}) \tag{13}$$

$$F_{ij}^k(\mathbf{R}) = \frac{\hbar^2}{M_k} \langle \psi_i(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}_k} | \psi_j(\mathbf{r}; \mathbf{R}) \rangle \tag{14}$$

$$G_{ij}(\mathbf{R}) = \sum_k \frac{\hbar^2}{2M_k} \langle \psi_i(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}_k}^2 | \psi_j(\mathbf{r}; \mathbf{R}) \rangle. \tag{15}$$

In contrast to H^e (eq. 5), in which T_N was omitted, H_{ij} is *not* diagonal in the basis of the adiabatic electronic wavefunctions (ψ_i). The individual electronic states are coupled *via* nuclear motions. Non-adiabatic coupling is the key player in a photochemical reaction, as we will show below.

In the limit that the electronic wavefunctions vary slowly with the nuclear dynamics, the off-diagonal non-adiabatic operators $F_{ij}^k(\mathbf{R})$ and $G_{ij}(\mathbf{R})$ are vanishingly small and can be safely neglected. Thus, the crux of the Born-Oppenheimer approximation is that H_{ij} is assumed to be diagonal everywhere:

$$H_{ij}(\mathbf{R}) = \left[T_N + V_i(\mathbf{R}) - \Lambda_{ij} \right] \delta_{ij}. \tag{16}$$

With this assumption the total molecular wavefunction becomes a product of a *single* nuclear and a *single* electronic wavefunction:

$$\Psi_i^{\text{tot}}(\mathbf{R}, \mathbf{r}) = \chi_i(\mathbf{R})\psi_i(\mathbf{r}; \mathbf{R}), \tag{17}$$

which implies that nuclear motion takes place on a *single* electronic potential energy surface $V_i(\mathbf{R})$ of a given electronic state i. In most of computational chemistry, the $\mathbf{\Lambda}$ is further assumed to be completely zero, which results in the adiabatic approximation:

$$H_{ij}(\mathbf{R}) = \left[T_N + V_i(\mathbf{R}) \right] \delta_{ij}. \tag{18}$$

The Born-Oppenheimer and adiabatic approximations not only reduce the computational complexity of the equations that have to be solved, but also provides a conceptually more intuitive picture of molecular structure and dynamics.

Conical Intersections

In regions of configuration space where the energy gaps between electronic states become comparable to the energy gaps between the vibrational states of the nuclei, resonance will occur between nuclear vibrations and electronic transitions. The populations of the adiabatic wavefunctions become strongly dependent on the nuclear dynamics and the non-adiabatic coupling operator ($\mathbf{\Lambda}$, eq. 13) can no longer be neglected. In regions of strong non-adiabatic coupling the Born-Oppenheimer approximation breaks down, and nucear dynamics induces population transfer between different electronic states, which is the origin of a radiationless transition. Furthermore, as we will demonstrate in this section, adiabatic potential energy surfaces can even intersect due to the coupling. These crossings provide efficient funnels for radiationless deactivation of the excited state and therefore play a crucial role in photochemistry.

In principle *all* electronic states $\psi_i(\mathbf{r}; \mathbf{R})$ are involved in the non-adiabatic coupling. However, in practice only states that are close in energy couple significantly. Therefore, the set of states included in the coupling can be truncated, reducing the dimension of the non-adiabatic coupling matrix $\mathbf{\Lambda}$.

The non-adiabatic coupling operators Λ_{ij} are non-local derivative operators that depend inversely on the energy gap between the coupled adiabatic states[3]:

$$F_{ij}^k(\mathbf{R}) = \frac{\hbar^2}{M_k} \langle \psi_i(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}_k} | \psi_j(\mathbf{r}; \mathbf{R}) \rangle = \frac{\hbar^2}{M_k} \frac{\langle \psi_i(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}_k} H^e | \psi_j(\mathbf{r}; \mathbf{R}) \rangle}{V_j - V_i} \tag{19}$$

As the gap $(V_j - V_i)$ narrows, coupling increases and the nuclear wavefunction that is initially on one surface will spread to another without losing energy, and a radiationless transition occurs.

If the surfaces become degenerate, *i.e.* $V_j - V_i = 0$, the coupling becomes infinite. Due to the non-local nature of the coupling matrix elements in the adiabatic representation, it is convenient to switch to a diabatic representation, in which the non-adiabatic coupling operator becomes a local, potential-like operator. The switch to the diabatic wavefunctions φ^{dia} is achieved by a unitary transformation of the adiabatic wavefunctions ψ^{adia} at each point in space[3]:

$$\varphi^{\text{dia}} = \mathbf{S}(\mathbf{R})\psi^{\text{adia}}. \tag{20}$$

From now on, we no longer use the superscripts dia and adia to indictate the diabatic φ and adiabatic ψ wavefunctions. In the diabatic representation the complete Hamiltonian (eq. 12) becomes

$$H_{ij}(\mathbf{R}) = T_N \delta_{ij} + W_{ij}(\mathbf{R}), \tag{21}$$

and the molecular Schrödinger equation 12 can be written in matrix notation as

$$\mathbf{H}\chi = [T_N \mathbf{1} + \mathbf{W}(\mathbf{R})]\chi = \mathbf{E}\chi, \tag{22}$$

in which $\mathbf{1}$ is the identity matrix, χ the vector of nuclear wavefunctions (χ_i, eqn 8), and $\mathbf{W}(\mathbf{R})$ is the diabatic potential energy matrix, which in contrast to the adiabatic potential matrix $\mathbf{V}(\mathbf{R})$, contains only *local* terms.

To illustrate the concept of the surface crossing, we consider a molecule in which there is coupling between two diabatic states A and B only. We can expand the potential matrix elements in a Taylor series around an arbitrary point $\mathbf{R}_0$:

$$\mathbf{W}(\mathbf{R} - \mathbf{R}_0) = \mathbf{W}^{(0)} + \mathbf{W}^{(1)} + \mathbf{W}^{(2)} + ... \tag{23}$$

At $\mathbf{R}_0$, we can choose the diabatic and adiabatic states to be equal. Then, the zero$^{\text{th}}$ order matrix, $\mathbf{W}^{(0)}$, is a diagonal matrix in which the elements correspond to the energies E_A, E_B of the diabatic states φ_A and φ_A at $\mathbf{R}_0$, which, by our choice of origin, are identical to the *adiabatic* energies V_1 and V_2:

$$\mathbf{W}^{(0)} = \frac{E_A + E_B}{2}\mathbf{1} + \begin{pmatrix} -\frac{E_B - E_A}{2} & 0 \\ 0 & \frac{E_B - E_A}{2} \end{pmatrix} = \mathbf{V}(\mathbf{R}_0) \tag{24}$$

For small displacements $\Delta\mathbf{R}$ around $\mathbf{R}_0$, the Taylor expansion in equation 23 can be truncated after the first order term

$$\mathbf{W}^{(1)} = \frac{\boldsymbol{\lambda} \cdot \Delta\mathbf{R}}{2}\mathbf{1} + \begin{pmatrix} -\frac{1}{2}\boldsymbol{\delta\kappa} \cdot \Delta\mathbf{R} & \boldsymbol{\kappa}^{AB} \cdot \Delta\mathbf{R} \\ \boldsymbol{\kappa}^{AB} \cdot \Delta\mathbf{R} & \frac{1}{2}\boldsymbol{\delta\kappa} \cdot \Delta\mathbf{R} \end{pmatrix}, \tag{25}$$

in which we have introduced linear potential constants that are defined as

$$\begin{aligned}
\boldsymbol{\delta\kappa} &\equiv \nabla_{\mathbf{R}}(E_B - E_A)|_{\mathbf{R_0}} \\
\boldsymbol{\kappa}^{AB} &\equiv \nabla_{\mathbf{R}}\langle\varphi_A|H^e|\varphi_B\rangle|_{\mathbf{R_0}} \\
\boldsymbol{\lambda} &\equiv \nabla_{\mathbf{R}}(E_A + E_B)|_{\mathbf{R_0}}
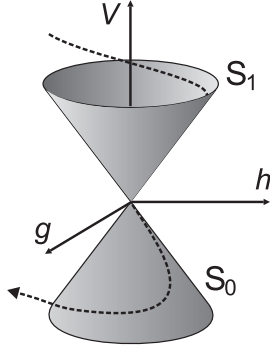\end{aligned} \tag{26}$$

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Figure 1: A conical intersection plotted in the 2-dimensional branching space that is spanned by the gradient difference vector (g) and the derivative coupling vector (g). Motion away from the intersection in the g-h plane lifts the degeneracy between the two electronic states S_1 and S_0. The dotted line shows a path of a nuclear trajectory passing from one electronic state (S_1) to another (S_0) through the intersection funnel.

We now choose $\mathbf{R}_0$ to be the point of degeneracy, where E_A and E_B are equal. Under this condition, $\mathbf{W}^{(0)}$ becomes a constant that we conveniently set to zero. The adiabatic potential energy surfaces V_1 and V_2 are obtained by diagonalizing the diabatic potential matrix $\mathbf{W}$. Thus for the two-state system considered here,

$$V_{1,2} = \frac{1}{2}\boldsymbol{\lambda} \cdot \boldsymbol{\Delta}\mathbf{R} \pm \frac{1}{2}\sqrt{[\boldsymbol{\delta\kappa} \cdot \boldsymbol{\Delta}\mathbf{R}]^2 + 4[\boldsymbol{\kappa}^{AB} \cdot \boldsymbol{\Delta}\mathbf{R}]} \tag{27}$$

The necessary condition for a crossing between the two potential energy surfaces at $\mathbf{R}_0$ is that the two electronic energies are identical. Therefore, two conditions need to be fulfilled simultaneously:

$$\begin{aligned}
\boldsymbol{\delta\kappa} \cdot \boldsymbol{\Delta}\mathbf{R} &= 0 \\
\boldsymbol{\kappa}^{AB} \cdot \boldsymbol{\Delta}\mathbf{R} &= 0.
\end{aligned} \tag{28}$$

Thus, to first order, the degeneracy is lifted in the two-dimensional space spanned by the vectors $\boldsymbol{\delta\kappa}$ and $\boldsymbol{\kappa}^{AB}$, known as the gradient difference vector and derivative coupling vector, respectively. The space spanned by these two vectors is often referred to as the branching space, or g-h plane. Furthermore, as is evident from equation 27 and illustrated in Fig. 1, the topology of the surfaces is that of a double cone, with the point of degeneracy at the apex. Orthogonal to the two-dimensional branching space exists the so-called intersection space (or seam space), in which the energies of the two states remain degenerate to first order. In a molecule with N internal degrees of freedom, the intersection space thus forms an $N - 2$ dimensional seam, each point of which is a conical intersection. If a molecules has less than two degrees of freedom, the two conditions for degeneracy (eq. 28) cannot be simultaneously fulfilled. Therefore in diatomic molecules states of the same symmetry do not cross, which was formulated by Von Neumann and Wigner[4].

The concept of the intersection seam is illustrated in Figure 2 for a hypothetical tri-atomic molecule. In our model system there are three internal degrees of freedom: two bond lengths (x_1 and x_2) and one angle (α), which are sufficient to define the configuration of the molecule.
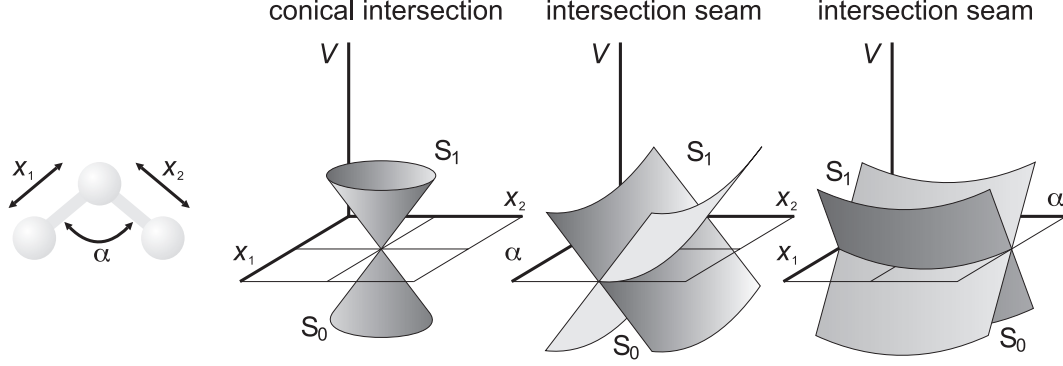
Figure 2: Surface crossing between two potential energy surfaces S_1 and S_0 in a hypothetical tri-atomic molecule (left). We let x_1 and x_2 be parallel to the gradient difference vector and the derivative coupling vector, respectively, and α be the remaining degree of freedom. When projected onto the branching space spanned by x_1 and x_2, the surfaces of S_0 and S_1 intersect in a single point, the conical intersection. In the two other subspaces, spanned by either x_2 and α, or by x_1 and α, there is an intersection line between the surfaces. In the second plot x_1 and in the third x_2 are assumed to be at their conical intersection coordinates.

Since *two* degrees of freedom are required to span the branching space, there is only *one* degree of freedom available to form the intersection seam. In our simple model system we let the branching space coordinates (*i.e.* the gradient difference and derivative coupling vectors) coincide with the two bond length variables x_1 and x_2. In reality, the branching space coordinates are usually more complex linear combinations of the three internal degrees of freedom.

The first plot in Figure 3 shows the two adiabatic potential energy surfaces (denoted S_0 and S_1) in the branching space. When projected onto this space, the surfaces adopt a double cone shape with a single intersection point at the apex. Any displacement away from the apex in either the x_1 or x_2 coordinate lifts the degeneracy.

The second plot shows the surfaces in the subspace spanned by the derivative coupling vector x_2 and the third independent degree of freedom, the bond angle α. The gradient difference vector x_1 is kept fixed at the conical intersection. Therefore, the only coordinate that can lift the degeneracy is x_2. If the latter is at the conical intersection as well, the surfaces intersect irrespective of the value of the angle variable (α). The intersection seam is thus a one-dimensional line that is parallel to α.

The third plot shows the projection of the two surfaces onto the subspace spanned by the gradient difference vector x_1 and the bond angle variable α. The derivative coupling vector x_2 is constrained to be at the conical intersection. Under this condition, only x_1 can lift the degeneracy and the surfaces intersect along a seam parallel to α.

The conical intersection has a number of peculiar characteristics. If we consider a small displacement $\mathbf{q}$ away from the cone tip in the branching plane, the diabatic energy matrix $U_{A,B}$ becomes

$$U_{A,B}(\mathbf{q}) = \begin{pmatrix} H_{AA}(\mathbf{q}) & H_{AB}(\mathbf{q}) \\ H_{AB}(\mathbf{q}) & H_{BB}(\mathbf{q}) \end{pmatrix} = S(\mathbf{q})\mathbf{1} + \begin{pmatrix} -\Delta H(\mathbf{q}) & H_{AB}(\mathbf{q}) \\ H_{AB}(\mathbf{q}) & \Delta H(\mathbf{q}) \end{pmatrix} \tag{29}$$

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with (see eq. 25)

$$\Delta H(\mathbf{q}) = \frac{H_{BB}(\mathbf{q}) - H_{AA}(\mathbf{q})}{2} = \boldsymbol{\delta\kappa} \cdot \mathbf{q}$$

$$H_{AB}(\mathbf{q}) = \boldsymbol{\kappa}^{AB} \cdot \mathbf{q} \tag{30}$$

$$S(\mathbf{q}) = \frac{H_{BB}(\mathbf{q}) + H_{AA}(\mathbf{q})}{2}$$

The matrix $U_{A,B}(\mathbf{q})$ is the two-state Hamiltonian matrix defined in the basis of the eigenvectors at the reference point, $\mathbf{R}_0$, at which the diabatic and adiabatic bases are identical. The diabatic potential matrix $U_{A,B}(\mathbf{q})$ can be diagonalized by the rotation matrix $\mathbf{T}(\mathbf{q})$[5], to obtain the adiabatic energies $V_{1,2}$

$$\mathbf{T}(\mathbf{q}) = \begin{pmatrix} \cos[\theta(\mathbf{q})] & -\sin[\theta(\mathbf{q})] \\ \sin[\theta(\mathbf{q})] & \cos[\theta(\mathbf{q})] \end{pmatrix} \tag{31}$$

From equation 30, the rotation angle $\theta(\mathbf{q})$ is defined as[5,6,7,8,9,10]:

$$\theta(\mathbf{q}) = \frac{1}{2}\arctan\left[\frac{2H_{AB}(\mathbf{q})}{\Delta H(\mathbf{q})}\right]$$

$$= \frac{1}{2}\arctan\left[\frac{2\boldsymbol{\kappa}^{AB}\cdot\mathbf{q}}{\boldsymbol{\delta\kappa}\cdot\mathbf{q}}\right] \tag{32}$$

$$= \frac{1}{2}\arctan\left[\frac{y}{x}\right]$$

where we have introduced the *scaled* coordinates x and y. Replacing these scaled coordinates by polar coordinates r and ϕ

$$r = \sqrt{x^2 + y^2}$$

$$\phi = \arctan\left[\frac{2y}{x}\right] \tag{33}$$

yields the following expression for the rotation angle

$$\theta(H_{AB}, \Delta H) = \frac{\phi}{2}. \tag{34}$$

Thus, a simple relationship exists between the polar angle (ϕ), which defines a rotation around the apex of the cone in the branching space on one hand, and the *mixing* angle (θ) for the diabatic states (φ_A, φ_B) on the other. Since the mixing depends *only* on the polar angle ϕ and *not* on the radius r, it is constant along any straight line with the origin at the apex of the double cone.

Because of this relationship, the adiabatic wavefunction changes sign upon a complete rotation around the apex of the cone in the branching space. This is demonstrated by comparing the wavefunctions at $\phi = \phi_0$ and $\phi = \phi_0 + 2\pi$. Substituting equation 34 into the rotation matrix (eq. 31) gives the following expression for the adiabatic states:

$$\psi_1 = \cos\left[\frac{\phi_0}{2}\right]\varphi_A - \sin\left[\frac{\phi_0}{2}\right]\varphi_B \tag{35}$$

and

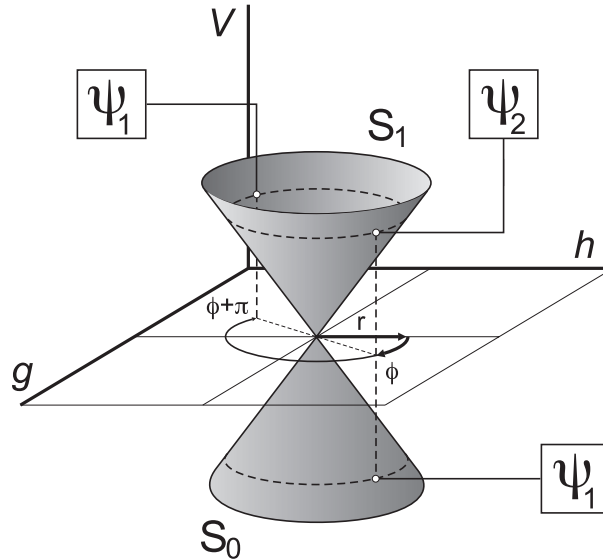$$\psi_2 = \sin\left[\frac{\phi_0}{2}\right]\varphi_A + \cos\left[\frac{\phi_0}{2}\right]\varphi_B. \tag{36}$$

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Figure 3: In the branching space (x,y), points lying on a circle with a small radius r and centered at the apex of the double cone are *diabatically* related. If we select a point on one of the surfaces and move it to the opposite side of the circle ($\phi \rightarrow \phi + \pi$), its wavefunction becomes equal to the wavefunction of the other surface at the original position. If we complete the circle, the point is back at its original position, but its wavefunction has changed sign (not shown, see text).

Next, we substitute $\phi = \phi_0 + 2\pi$ to show that the adiabatic wavefunction has indeed changed sign after the 360° rotation:

$$\psi_1 = \cos\left[\frac{\phi_0 + 2\pi}{2}\right]\varphi_A - \sin\left[\frac{\phi_0 + 2\pi}{2}\right]\varphi_B = \sin\left[\frac{\phi_0}{2}\right]\varphi_A - \cos\left[\frac{\phi_0}{2}\right]\varphi_B = -\psi_1 \quad (37)$$

Because single-valuedness of the wavefunction is one of the basic postulates of quantum mechanics, this result implies that the conical intersection is a singularity. This singularity is a consequence of the separation between electronic and nuclear degrees of freedom, which is not valid near surface crossings. Thus, the singularity only exists for the adiabatic electronic wavefunction and is remedied by the nuclear wavefunction, so that the total molecular wavefunction is single-valued function. Furthermore, as illustrated schematically in Figure 3, rotation by 90° permutes the order of the electronic states, as is demonstrated by substituting $\theta + \pi$ into equation 34:

$$\psi_1 = \cos\left[\frac{\phi_0 + \pi}{2}\right]\varphi_A - \sin\left[\frac{\phi_0 + \pi}{2}\right]\varphi_B = \sin\left[\frac{\phi_0}{2}\right]\varphi_A - \cos\left[\frac{\phi_0}{2}\right]\varphi_B = -\psi_2 \quad (38)$$

The conical intersection seam is the central mechanistic feature in a photochemical reaction. The conical intersection provides a funnel for efficient radiationless decay between electronic states (Figure 1). To illustrate the relationship between the surface crossing and photochemical reactivity, we can draw a parallel with the transition state in ground state chemistry. The transition state forms the bottleneck through which the reaction must pass on its way from reactants to products. A transition state separates the reactant and product energy minima along the reaction path. A conical intersection also forms a bottleneck that separates the excited state branch of

the reaction path from the ground state branch. The crucial difference between conical intersections and transition states is that, while the transition state must connect the reactant minimum to a single product minimum *via* a single reaction path, an intersection is a spike on the ground state energy surface and thus connects the excited state reactant to two or more products on the ground state *via* several reaction paths.

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