

Is the Breakdown of the Born-Oppenheimer Approximation Responsible for Internal Conversion in Large Molecules?*

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Abstract. Vibronic radiationless transitions in large polyatomic molecules can be thought of as a process whereby the molecule, initially prepared in a discrete *quasistationary* state, makes a transition to an adjoining vibronic continuum belonging to a lower electronic state of the same multiplicity. In many instances the transition is analogous to penetration through a barrier between two "nested" potential sheets far away from an actual intersection of the sheets. Simultaneous distortions of vibrational and electronic parts of the wavefunction are required for such a tunneling process. The vibrational distortion manifests itself in the familiar Franck-Condon effect. The electronic distortion can be caused by nontotally symmetric vibrations of the molecule either because of the displaced nuclear configuration, to which the electrons instantly respond (Herzberg-Teller effect), or because of the protracted response of the electrons to the kinetic energy of nuclear motion (nonadiabatic effect or the breakdown of the Born-Oppenheimer approximation). It is found here that Herzberg-Teller coupling is more effective in causing radiationless transitions than the breakdown of the Born-Oppenheimer approximation when the potential surfaces involved are not close to an intersection.

Introduction. Current theories¹⁻⁷ of vibronic radiationless transitions in large molecules having many vibrational degrees of freedom are based upon the same concepts as are well-established theories of spontaneous processes in atoms (Auger effect,⁸ autoionization⁹), diatomic molecules (predissociation¹⁰), and atomic nuclei (emission of internal conversion electrons and β -decay¹¹). Emission and absorption of radiation can be discussed in the same way.^{12, 13} For all of these processes one envisions in zero order a discrete state of an atom, molecule, or nucleus embedded in a continuum. Energy-conserving transitions occur in the over-all system through *time-independent* coupling between the discrete state and the continuum.¹⁴

The discrete state for the vibronic radiationless transition process is a vibrational level belonging to a certain excited electronic state of the molecule, while the adjacent (quasi)-continuum corresponds to a lower electronic state with a large amount of vibrational excitation.^{1, 2} The vibrational excitation may be purely intramolecular if the molecule is sufficiently large^{2, 5, 6} or it may be a combination of internal and external vibrations in the case where a smaller

molecule is surrounded by an "environment."¹ If the two electronic states are singlet states, electron spin can be neglected and the transition from the discrete state into the adjoining continuum is called *internal conversion*¹⁵ by molecular spectroscopists. If the multiplicity is different in the two electronic states, the process is known as *intersystem crossing*.¹⁵ It is well known that for all of these processes, to a good approximation,^{1, 5, 13} the decay of the initial state is exponential, with a transition probability per unit time,

$$k = (2\pi/\hbar)\bar{\rho}(E)\beta^2F. \quad (1)$$

The term β^2 is a coupling term, F is a Franck-Condon factor, and $\bar{\rho}(E)$ is the effective density of quasicontinuum states.

Emphasis in the past has been placed primarily on the many interesting manifestations of the Franck-Condon factor in equation (1).^{1, 2, 4, 7} Recently, however, much discussion has revolved around the detailed nature of the coupling between the initial and final states.^{3, 5, 7} In this paper we shall show that the vibronic coupling for the internal conversion process need not be associated with the nuclear kinetic energy operator as is widely supposed. We suggest an alternate explanation for this coupling when the potential surfaces are fairly far removed from an actual intersection.

The Born-Oppenheimer approximation: The usual approach³⁻⁵ to vibronic coupling in the radiationless transition problem is to start off with a Hamiltonian,

$$H_{B.O.} = \mathcal{H} - \mathcal{J}(Q) - H_{rad}, \quad (2)$$

where \mathcal{H} is the full Hamiltonian, H_{rad} is the interaction of the molecule with the quantized radiation field, and $\mathcal{J}(Q)$ represents the sum over-all nuclear kinetic energy operators. In equation (2) it is assumed that no external fields are provided during the time of observation of the nonradiative process¹⁶ and thus that H_{rad} pertains only to spontaneous emission.

Vibronic eigenfunctions of $H_{B.O.}$ are constrained to have the form¹⁷

$$\Psi_{B.O.}^{kr} = \varphi_k(q, Q)\chi_{kr}(Q), \quad (3)$$

where q and Q represent collective coordinates for the electrons and nuclei, respectively; k is a quantum number that labels the electronic state; and $\chi_{kr}(Q)$ is the r th vibrational eigenfunction belonging to this electronic state. The functions φ and χ can then readily be shown¹⁷ to be solutions of

$$H_{B.O.}\varphi_k(q, Q) = E(Q)\varphi_k(q, Q), \quad (4)$$

$$\{E(Q) + \mathcal{J}(Q) + \langle \varphi_k | \mathcal{J}(Q) | \varphi_k \rangle\}\chi_{kr}(Q) = W_{kr}\chi_{kr}(Q), \quad (5)$$

the first being the "electronic Schrödinger equation," the second the "vibrational Schrödinger equation." In equation (5), W_{kr} is the total energy of the kr th vibronic state while $E(Q)$ contains the electronic energy as a function of nuclear displacements as well as nuclear-nuclear repulsion terms. $E(Q)$ along with the usually small first-order energy term $\langle \varphi_k | \mathcal{J}(Q) | \varphi_k \rangle$ therefore represents the potential energy function under whose influence the nuclei move.

It seems to have been almost universally assumed³⁻⁵ that the Born-Oppen-

heimer states $\varphi_k(q, Q)\chi_{kr}(Q)$ are the quasistationary states that should be considered the ones initially "prepared" in the internal conversion process. In other words, the discrete vibronic state and the neighboring quasicontinuum have in the past all been assumed to be eigenstates of $H_{B.o.}$. When this assumption is made, it is obvious that such eigenstates are nonstationary since one has omitted from $H_{B.o.}$ the effect of nuclear velocities on the functions $\varphi_k(q, Q)$, only the effect of instantaneous nuclear positions having been considered. Thus, off-diagonal elements of the total Hamiltonian matrix exist in the Born-Oppenheimer representation between states of different k and r . These off-diagonal elements certainly would lead to internal conversion if it were true that the actual initial state is indeed a pure Born-Oppenheimer state. In fact, in the Born-Oppenheimer representation this would be the only source responsible for the radiationless process, since, besides H_{rad} , the nuclear kinetic energy operators are the only terms omitted from \mathcal{H} in forming $H_{B.o.}$. The question exists, however, "Do the Born-Oppenheimer states really have physical significance for the problem at hand or is their significance merely historical?"

Choice of perturbation Hamiltonian: As far as we can see there is no *a priori* reason for choosing Born-Oppenheimer states as a starting point in the calculation of radiationless rates. The choice of zero-order Hamiltonian is by no means arbitrary, however. Neither is the choice fixed until one fixes interest upon a specific problem. The description of the zero-order states is totally "dictated by the conditions under which experimental observations are to be made on the system."¹⁸ Even though the time scale for our problem here is much longer than that usually associated with the formation of Born-Oppenheimer states, we shall show that these states really are in the process of forming during the radiationless transition and therefore are inappropriate zero-order states for the problem.

What then are the zero-order states appropriate for discussion of internal conversion, and more generally, is there some systematic manner by which one can go about choosing the appropriate zero-order states for a given problem? The answer to the second part of this question involves a critical dissection of the total Hamiltonian. Different parts of the Hamiltonian correspond to different nonradiative processes depending upon their magnitude and upon the coordinate-mixing they give rise to. *But extreme caution must be exercised so that the mistake is not made of including the relevant perturbing part of the Hamiltonian in the zero-order problem to begin with!* If this is inadvertently done the correct transition probability can be obtained only by treating these zero-order eigenfunctions by a stationary-state approach.¹⁹ Totally wrong results would be obtained by unconsciously setting up the problem as a coupling among such inappropriately chosen zero-order states caused by the irrelevant perturbation Hamiltonian. This we believe is just the situation that arises if one attempts to use Born-Oppenheimer states as zero-order states in the present problem.

The proper dissection of the Hamiltonian: To describe the radiationless decay of a molecule from a discrete state to a quasi-continuum of states, we separate the total Hamiltonian into two parts: a *zero-order part* that includes terms corresponding to processes that happen much faster than the time scale of the

radiationless decay and a *perturbation* or *scattering term* that takes the system from one zero-order eigenstate to another during the experimental time.

If the interaction terms due to the environment do not appear,^{1, 2, 5, 6} then the total Hamiltonian \mathcal{H} in a molecule-fixed coordinate system is

$$\mathcal{H} = \mathcal{J}(q) + \mathcal{J}(Q) + \mathcal{V}(q) + \mathcal{V}(q, Q) + \mathcal{V}(Q) + H_{\text{rad}}, \quad (6)$$

where $\mathcal{J}(q)$ is the electronic kinetic energy operator, $\mathcal{J}(Q)$ the nuclear kinetic energy operator, $\mathcal{V}(q)$ the electron-electron Coulomb energy, $\mathcal{V}(Q)$ the nuclear-nuclear Coulomb energy, and $\mathcal{V}(q, Q)$ is the nuclear-electronic Coulomb energy summed over all the electrons and/or nuclei in the molecule.

Even though virtually all terms will eventually be retained, it is convenient to think of the nuclear-electronic Coulomb energy $\mathcal{V}(q, Q)$ as a Taylor's series expanded about some nuclear equilibrium configuration Q_0 ($Q_i = 0$, for all Q_i):

$$\mathcal{V}(q, Q) = \mathcal{V}(q, Q_0) + \sum_i \left(\frac{\partial \mathcal{V}}{\partial Q_i} \right)_0 Q_i + \dots, \quad (7)$$

Later we will wish to remove one or more linear terms of the form $(\partial \mathcal{V} / \partial Q_p)_0 Q_p$ from the total Hamiltonian, where Q_p , a "promoting mode,"²⁰ represents a particular nuclear displacement responsible for the coupling. For these promoting modes it is illuminating to visualize initially that in both the ground and excited states the equilibrium positions are identical, the restoring forces only being different. An oscillator such as this is referred to as being "distorted" but not "displaced" and plays a leading role in the theory of vibronic coupling in polyatomic molecules.⁴ It is stressed, however, that the qualitative arguments presented in this paper do not depend on the complete absence of "displacement." A moderate displacement is tolerable so long as it does not lead to potential surface crossing and will simply cause the theory to be a little more cumbersome without altering the basic conclusions.

Note that up to now there has been no need to fall back on the harmonic oscillator approximation for the vibrations. However, it will certainly be theoretically convenient if we can assume that Q_p is represented by a certain normal mode of the molecule in the harmonic approximation. Until actual calculations are performed, no such assumption is necessary about the other so-called "accepting modes," which enter only into the Franck-Condon factors.

As mentioned earlier, the molecule has time to form well-established vibrational states before the emission process occurs.²¹ The minimum Hamiltonian that we can write and still permit the formation of bound vibrational states is:

$$H_0 = \mathcal{H} - \mathcal{J}(Q) - [\mathcal{V}(q, Q) - \mathcal{V}(q, Q_0)] - H_{\text{rad}}. \quad (8)$$

This Hamiltonian gives rise to vibronic wavefunctions of the form¹⁷

$$\Psi_0^{kr} = \varphi_k(q, Q_0) \chi_{kr}(Q), \quad (9)$$

where the functions φ and χ are solutions of

$$H_0 \varphi_k(q, Q_0) = E^0(Q_0) \varphi_k(q, Q_0), \quad (10)$$

$$[E^0(Q) + \mathcal{J}(Q)] \chi_{kr}(Q) = W_{kr} \chi_{kr}(Q). \quad (11)$$

Here the "nuclear potential energy function" $E^0(Q)$ in equation (11), which contains the neglected Q -dependent part of the Hamiltonian [$\mathcal{U}(q, Q) - \mathcal{U}(q, Q_0)$] as a first-order energy correction term, is given by

$$E^0(Q) = \langle \varphi_k(q, Q_0) | \mathcal{H} - H_{\text{rad}} - \mathcal{V}(Q) | \varphi_k(q, Q_0) \rangle. \quad (12)$$

It is with respect to this function that the equilibrium nuclear position necessary for the expansion in equation (7) is defined. The wavefunctions in this approximation are known as *clamped nuclei* or *crude Born-Oppenheimer wavefunctions*.¹⁷ In the following discussion we will ignore H_{rad} , since in the present problem it usually merely opens up independent alternative channels through which the excited state may decay.

The relative magnitude of two possible coupling terms: First consider the matrix element β that is obtained by using [$\mathcal{U}(q, Q) - \mathcal{U}(q, Q_0)$] as a perturbation. We will assume that only one displacement Q_p is directly involved in coupling the two electronic states φ_k and φ_l , and for convenience we will assume that Q_p represents a normal mode in the harmonic approximation. Q_p is thus the promoting mode and need possess only one quantum of excitation energy. The other types of nuclear displacements, the "accepting modes," because of symmetry or other reasons, are assumed to be incapable of coupling initial and final states. They are highly excited and contribute to the radiationless process only through the Franck-Condon factor F in equation (1). Since the "accepting modes" are not directly involved in the coupling, we will include them in our zero-order Hamiltonian. This results in a much less crude approximation than does the Hamiltonian H_0 of equation (8). This Hamiltonian becomes

$$H_{\text{H.T.}} = \mathcal{H} - \mathcal{V}(Q) - (\partial\mathcal{U}/\partial Q_p)_0 Q_p, \quad (13)$$

where as we mentioned earlier, only one linear term in the expansion of $\mathcal{U}(q, Q)$ has been extracted from the full Hamiltonian. Terms quadratic and higher in the expansion are assumed to give a negligible contribution to the radiationless transition rate.²² As before they are included in the first-order energy correction to give rise to bound vibrational levels associated with the coordinate Q_p .

The Hamiltonian given by equation (13) has been labeled with the subscript H.T. because of the obvious similarities between this mechanism for radiationless transitions and Herzberg-Teller vibronic coupling for symmetry-forbidden radiative processes.²³ The eigenfunctions of equation (13) are

$$\Psi_{kr}^{\text{H.T.}} = \varphi_k^{\text{H.T.}}(q, Q \neq Q_p) \chi_{kr}(Q) \quad (14)$$

and are solutions of Schrödinger equations similar to equations (10) and (11). The matrix element $\beta_{\text{H.T.}}$ describing the coupling due to the promoting mode Q_p is

$$\begin{aligned} \beta_{\text{H.T.}} &= \langle \Psi_{kr}^{\text{H.T.}} | (\partial\mathcal{U}/\partial Q_p)_0 Q_p | \Psi_{Hl}^{\text{H.T.}} \rangle \\ &= \langle \varphi_k^{\text{H.T.}} | (\partial\mathcal{U}/\partial Q_p)_0 | \varphi_l^{\text{H.T.}} \rangle \langle \chi_{kr} | Q_p | \chi_{ls} \rangle. \end{aligned} \quad (15)$$

Note that Herzberg-Teller vibronic coupling occurs entirely within the framework of the Born-Oppenheimer approximation. If we treat the mixing between

the eigenstates in equation (14) to all orders in Q_p , the wavefunction we finally obtain is the exact Born-Oppenheimer wavefunction of (3).

Suppose that in equation (15) instead of treating the term $(\partial\mathcal{U}/\partial Q_p)_0 Q_p$ as the perturbation term, we were to use the term $\mathfrak{J}(Q_p)$ also neglected in (8). Recall that we have assumed only one nuclear displacement Q_p to be responsible for the vibronic coupling. In this case the matrix element $\langle\Psi_{\text{H.T.}}^{kr}|\mathfrak{J}(Q_p)|\Psi_{\text{H.T.}}^{\ell s}\rangle$ is zero since the Herzberg-Teller electronic wavefunctions do not depend on Q_p . However, the matrix element that arises when the neglected nuclear kinetic energy term (from Eq. (2)) is used as a perturbation with the Born-Oppenheimer wavefunctions (Eq. (3)) is

$$\beta_{\text{B.O.}} = \langle\Psi_{\text{B.O.}}^{kr}|\mathfrak{J}(Q_p)|\Psi_{\text{B.O.}}^{\ell s}\rangle, \quad (16)$$

which is nonzero since the Born-Oppenheimer electronic wavefunctions do depend on Q_p .

To get a rough idea of the relative magnitude of these two matrix elements, we can derive a simple approximate expression for their ratio $\beta_{\text{B.O.}}/\beta_{\text{H.T.}}$. We write to first order the Born-Oppenheimer electronic wavefunction in terms of the Herzberg-Teller functions⁵

$$\varphi_k(q, Q) = \varphi_k^{\text{H.T.}} + \sum_{\ell} \frac{\langle\varphi_k^{\text{H.T.}}|(\partial\mathcal{U}/\partial Q_p)_0|\varphi_{\ell}^{\text{H.T.}}\rangle Q_p}{\Delta E_k} \varphi_{\ell}^{\text{H.T.}} \quad (17)$$

Note that the only perturbing term we need to consider in writing equation (17) is the linear term in Q_p since except for this one term $H_{\text{B.O.}}$ and $H_{\text{H.T.}}$ are identical. If it is now further assumed that the vibrational wavefunctions χ_{kr} can be written as a product of harmonic oscillator functions

$$\chi_{kr}(Q) = \prod_{\gamma} x_{\gamma}^{kr}. \quad (18)$$

One then obtains an expression for $\beta_{\text{B.O.}}$ similar to the one previously derived by Bixon and Jortner⁵

$$\beta_{\text{B.O.}} = -\hbar^2 \frac{\langle\varphi_k^{\text{H.T.}}|(\partial\mathcal{U}/\partial Q_p)_0|\varphi_{\ell}^{\text{H.T.}}\rangle}{\Delta E_{\ell k}} \langle x_p^{kr}|\partial/\partial Q_p|x_p^{\ell s}\rangle \prod_{\gamma \neq p} \langle x_{\gamma}^{kr}|x_{\gamma}^{\ell s}\rangle, \quad (19)$$

and the Herzberg-Teller matrix element simply becomes

$$\beta_{\text{H.T.}} = \langle\varphi_k^{\text{H.T.}}|(\partial\mathcal{U}/\partial Q_p)_0|\varphi_{\ell}^{\text{H.T.}}\rangle \langle x_p^{kr}|Q_p|x_p^{\ell s}\rangle \prod_{\gamma \neq p} \langle x_{\gamma}^{kr}|x_{\gamma}^{\ell s}\rangle. \quad (20)$$

Their ratio is

$$\frac{\beta_{\text{B.O.}}}{\beta_{\text{H.T.}}} = \frac{-\hbar^2 \langle x_p^{kr}|\partial/\partial Q_p|x_p^{\ell s}\rangle}{\Delta E_{\ell k} \langle x_p^{kr}|Q_p|x_p^{\ell s}\rangle}. \quad (21)$$

Equation (21) can be simplified still further if we assume that the radiationless process occurs from a vibrationally unexcited level of the initial electronic state and we recall that the normal mode Q_p is a distorted but undisplaced mode. In this case, evaluating the integrals in the harmonic approximation,²⁴

$$\frac{\beta_{\text{B.O.}}}{\beta_{\text{H.T.}}} = \frac{f_p \hbar \omega_p}{\Delta E_{\text{elec}}}, \quad (22)$$

where f_p is the ratio of the vibrational frequency of the p th normal mode Q_p in the initial and final electronic states, $f = \nu_{\text{initial}}/\nu_{\text{final}}$; f is approximately unity in most cases.²⁵ $\hbar\omega_p$ is the vibrational energy quantum for the final state and $\Delta E_{\text{elec.}}$ is the *purely electronic energy difference* between the interacting states; i.e., $\Delta E_{\text{elec.}}$ is the vertical energy difference between potential surfaces in the lower and vibrationally unexcited upper electronic states.

Typically, vibrational quanta are on the order of 1000 cm^{-1} and $\Delta E_{\text{elec.}}$ is generally in the vicinity of $10,000 \text{ cm}^{-1}$. Equation (22) thus implies that $\beta_{\text{B.O.}}/\beta_{\text{H.T.}}$ is on the order of 0.1 and that Herzberg-Teller coupling is 100 times more effective at inducing a radiationless process between Herzberg-Teller states than is the breakdown of the Born-Oppenheimer approximation between Born-Oppenheimer states. Such slow transitions among Born-Oppenheimer states cannot be detected because long before these transitions occur the discrete Herzberg-Teller state has decayed into the Herzberg-Teller continuum and the "experiment" is completed. In other words the radiationless process corresponds to the *formation* of a Born-Oppenheimer state, not to a transition between Born-Oppenheimer states.

Equation (22) serves to emphasize another important point. The vibronic radiationless process has long¹ been envisioned as a *tunneling* process between two nonintersecting potential energy surfaces. If an electronic degeneracy, i.e., a potential surface intersection, should occur, then our treatment would be inadequate since $\Delta E_{\text{elec.}}$ would be zero. The case of molecular radiationless transitions involving potential crossing was discussed many years ago by Teller²⁶ with respect to predissociation in diatomic molecules. For such processes Herzberg-Teller vibronic coupling is completely inappropriate.

Conclusions. The point emphasized here is that there is no *a priori* reason for assuming that these radiationless processes must be due to a breakdown of the Born-Oppenheimer approximation. Other channels exist and should be given equal attention when radiationless processes are discussed. We believe that the approximations made in deriving equation (21) are reasonable for most molecules and, therefore, that in most cases, Herzberg-Teller coupling is stronger than coupling due to the Born-Oppenheimer breakdown. Recent attempts to calculate the vibronic coupling in the radiationless transition problem using the breakdown of the Born-Oppenheimer approximation have indeed given results approximately two orders of magnitude too small.²⁷

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²¹ The molecule not only has time to form discrete vibrational levels but in most cases it also has time to reach thermal equilibrium among these vibrational states before emission occurs.

²² There may, of course, be cases where more than one normal coordinate is effective at providing the requisite coupling. These cases also occur in Herzberg-Teller theory²³ and can be treated by summing the transition probabilities over all the promoting modes. It is also possible that the totality of higher order terms in the expansion of $\mathcal{U}(q, Q)$ may contribute significantly to the coupling. We have assumed for simplicity that these terms are negligible since they seem to be negligible in the Herzberg-Teller coupling problem.

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