Potential Energy Surfaces and Effects on Electronic and Raman Spectra

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The Born-Oppenheimer (BO) approximation (*1, 2*) leads to the separation of the electronic motion from the motion of the nuclear framework. The motion of the nuclear framework can further be separated into rotational and vibrational motions. The basis of the separations is still in debate (*3, 4*), but we shall not delve into this. The fact is that, in most cases, the energy levels of molecules can be interpreted as rotational, vibrational, or electronic in origin.

The BO approximation is already very well known and widely used (*5, 6*) in the study of the properties of molecules in the ground electronic state. Associated with the BO approximation is a plethora of terms and concepts—potential energy surfaces, Herzberg-Teller (HT) coupling, BO coupling, adiabatic approximation, nonadiabatic approximation, Jahn-Teller effect, Renner-Teller effect, etc.—which can be quite confusing, not to mention complicated. There is a need to present a unified treatment on this subject. However, no short article can do justice to the enormous literature that has accumulated. Ballhausen and Hansen (*7*) have pointed out some of the confusion in the BO approximation. This present article will only touch briefly on one aspect of the BO approximation—the potential energy surfaces—and can be viewed as complementary to ref. (*7*).

Recently, in electronic (*8, 9*), ordinary and resonance Raman (*9–15*), and multiphoton spectroscopies (*16*) involving the excited states of molecules, the BO approximation has been used as a starting point to interpret the results. Such processes involve not only the ground, but also the excited electronic states. It is fair to say that a lot is known about the ground electronic state already, and we are just beginning to probe the richer excited electronic states. In the BO approximation, a vibronic process consists of an initial instantaneous Franck-Condon transition from an initial to a final electronic state, followed by a relaxation of the nuclear framework on the final potential energy surface. The theoretical descriptions of these processes require, first, the nuclear coordinate dependence in the electronic wavefunctions. This is necessary in order to determine the nuclear coordinate dependence of the electronic transition dipole moments. However, this problem is commonly swept under the rug by assuming the Condon approximation of constant transition dipole moment. We shall not address this problem here. Secondly, there is a need to know the form and orientation of the excited state potential energy surface relative to the initial potential energy surface. This provides information on how the nuclear framework will relax when it is placed in the excited electronic state. The potential energy surface is central to the study of molecular dynamics—one of the most interesting areas of molecular spectroscopy today. We shall focus on the potential energy surfaces, and derive some simple results that have important consequences.

We begin with a discussion of the Born-Oppenheimer approximation, and accompanying results. We then look at the simplest case of isolated, nondegenerate electronic states, and see how the potential energy surfaces are oriented relative to each other. Finally, we discuss some implications of the results for electronic and Raman spectroscopies.

Born-Oppenheimer Results

In the description of polyatomics, it is common to treat the rotational motion separately, and consider the interaction of the electronic and vibrational motions. To do this it is necessary to introduce a set of axes, known as molecule fixed axes, attached to the nuclear framework and rotating with it (*17*). This set of axes has origin at the nuclear center of mass. It is assumed that the positions of the N nuclei deviate only by small amounts from some reference configuration. The molecule has a nuclear inertia tensor in the reference configuration, and the molecule fixed axes are oriented along the principal axes of the reference inertia tensor. This leads to a total of six constraints on the nuclear motion—three conditions corresponding to the absence of translations and three more for the absence of rotations. This leaves $3N - 6$ independent generalized coordinates, which we denote collectively by **q**, to describe the small nuclear vibrations. This is true for a nonlinear molecule. For a linear molecule, there are only two constraints for the absence of rotations, thus leaving $3N - 5$ independent generalized coordinates for the vibrations. Henceforth, to avoid repetition, we shall assume a nonlinear molecule with $3N - 6$ vibrational modes.

The moleculear vibronic Hamiltonian is given by,

$$\mathrm{H}(\boldsymbol{r},\boldsymbol{q}) = \mathrm{T}(\boldsymbol{r}) + \mathrm{U}(\boldsymbol{r},\boldsymbol{q}) + \mathrm{T}(\boldsymbol{q}) \tag{1}$$

where, in atomic units,

$$\mathrm{T}(\boldsymbol{r}) = -\frac{1}{2}\sum_i \frac{\partial^2}{\partial \boldsymbol{r}_i{}^2} \tag{2}$$

and

$$\mathrm{T}(\boldsymbol{q}) = -\frac{1}{2}\sum_a^{3N-6} \frac{\partial^2}{\partial q_a^2} \tag{3}$$

This consists of the electronic kinetic energy operator $\mathrm{T}(\boldsymbol{r})$; the kinetic energy operator for the nuclear vibrations $\mathrm{T}(\boldsymbol{q})$; and the total Coulomb potential energies $\mathrm{U}(\boldsymbol{r},\boldsymbol{q})$ of the electrons with internal coordinates $\boldsymbol{r}$ and the nuclei with generalized coordinates $\boldsymbol{q}$. In one view of the Born-Oppenheimer approximation, it is assumed that the faster moving, light electrons can adjust their motions instantaneously to the slow movements of the heavy nuclei. This allows us to solve first for the electronic motion using fixed nuclear coordinates. The electronic states $\phi_m(\boldsymbol{r},\boldsymbol{q})$ are thus assumed to satisfy the equation,

$$(\mathrm{T}(\boldsymbol{r}) + \mathrm{U}(\boldsymbol{r},\boldsymbol{q}))\phi_m(\boldsymbol{r},\boldsymbol{q}) = \mathrm{V}_m(\boldsymbol{q})\phi_m(\boldsymbol{r},\boldsymbol{q}) \tag{4}$$

for fixed nuclear configuration $\boldsymbol{q}$. The solution of eqn. (4) is a formidable problem even for one nuclear configuration $\boldsymbol{q}_0$, much less for the whole continuous range of $\boldsymbol{q}$. Suppose, however, that it has been possible to solve eqn. (4) for one reference configuration $\boldsymbol{q}_0$:

$$[\mathrm{T}(\boldsymbol{r}) + \mathrm{U}(\boldsymbol{r},\boldsymbol{q}_0)]\phi_m^0(\boldsymbol{r},\boldsymbol{q}_0) = V_m^0(\boldsymbol{q}_0)\phi_m^0(\boldsymbol{r},\boldsymbol{q}_0) \tag{5}$$

The reference configuration $\boldsymbol{q}_0$ is usually taken to be the equilibrium nuclear configuration in the ground electronic state. The complete set $\{\phi_m^0(\boldsymbol{r},\boldsymbol{q}_0)\}$ of electronic wavefunctions is commonly known as the crude Born-Oppenheimer (CBO) electronic basis set. This CBO basis set can be used to obtain the solutions to eqn. (4) for nuclear coordinates $\boldsymbol{q}$ in the neighborhood of $\boldsymbol{q}_0$, by the application of perturbation theory. For small nuclear displacements about $\boldsymbol{q}_0$, the Coulomb potential energy $\mathrm{U}(\boldsymbol{r},\boldsymbol{q})$ can be expanded in a Taylor series,

$$\mathrm{U}(\boldsymbol{r},\boldsymbol{q}) = \mathrm{U}(\boldsymbol{r},\boldsymbol{q}_0) + \sum_{a}^{3N-6}\left(\frac{\partial \mathrm{U}}{\partial q_a}\right)_{\boldsymbol{q}_0}(q_a - q_{a0}) + \frac{1}{2}\sum_{a,b}^{3N-6}\left(\frac{\partial^2 \mathrm{U}}{\partial q_a \partial q_b}\right)_{\boldsymbol{q}_0}(q_a - q_{a0})(q_b - q_{b0}) + \ldots \quad (6)$$

It is common (for analytical reasons) to retain only up to quadratic terms in **q**, and discuss the final potential energy surfaces for the nuclear motion in the harmonic approximation, because the wavefunctions and eigenenergies for the multidimensional harmonic oscillator are well known. This can sometimes lead to closed-form expressions, which eases the computations. Without loss of generality, $\mathbf{q}_0$ can be set equal to zero, and the electronic states, for **q** in the neighborhood of $\boldsymbol{q}_0 = 0$, are approximately given by the solutions to

$$[\mathrm{T}(\boldsymbol{r}) + \tilde{\mathrm{U}}(\boldsymbol{r},\boldsymbol{q})]\tilde{\phi}(\boldsymbol{r},\boldsymbol{q}) = \tilde{\mathrm{V}}(\boldsymbol{q})\tilde{\phi}(\boldsymbol{r},\boldsymbol{q}) \quad (7)$$

where

$$\tilde{\mathrm{U}}(\boldsymbol{r},\boldsymbol{q}) = \mathrm{U}(\boldsymbol{r},\boldsymbol{q}_0) + \sum_{a}^{3N-6}\left(\frac{\partial \mathrm{U}}{\partial q_a}\right)_0 q_a + \frac{1}{2}\sum_{a,b}^{3N-6}\left(\frac{\partial^2 \mathrm{U}}{\partial q_a \partial q_b}\right)_0 q_a q_b \quad (8)$$

The electronic wavefunctions $\tilde{\phi}(\boldsymbol{r},\boldsymbol{q})$ can be expanded in the CBO basis set,

$$\tilde{\phi}(\boldsymbol{r},\boldsymbol{q}) = \sum_{j=1}^{\infty} \mathrm{c}_j(\boldsymbol{q})\tilde{\phi}_j^0(\boldsymbol{r}) \quad (9)$$

Substituting this into eqn. (7), left multiplying with $\phi_i^{0*}(\boldsymbol{r})$ and integrating over the electronic coordinates $\boldsymbol{r}$, we obtain a set of equations for the unknown coefficients $\mathrm{c}_j(\boldsymbol{q})$. These can be written compactly in matrix notation as,

$$\begin{bmatrix} V_1^0 + \sum_a u_{11}^a q_a + \frac{1}{2}\sum_{a,b} u_{11}^{ab} q_a q_b - \tilde{\mathrm{V}}(\mathbf{q}) & \sum_a u_{12}^a q_a + \frac{1}{2}\sum_{a,b} u_{12}^{ab} q_a q_b & \cdots & \sum_a u_{1m}^a q_a + \frac{1}{2}\sum_{a,b} u_{1m}^{ab} q_a q_b & \cdots \\ \sum_a u_{21}^a q_a + \frac{1}{2}\sum_{a,b} u_{21}^{ab} q_a q_b & V_2^0 + \sum_a u_{22}^a q_a + \frac{1}{2}\sum_{a,b} u_{22}^{ab} q_a q_b - \tilde{\mathrm{V}}(\boldsymbol{q}) & \cdots & \sum_a u_{2m}^a q_a + \frac{1}{2}\sum_{a,b} u_{2m}^{ab} q_a q_b & \cdots \\ \vdots & \vdots & \vdots & \vdots & \\ \sum_a u_{m1}^a q_a + \frac{1}{2}\sum_{a,b} u_{m1}^{ab} q_a q_b & \sum_a u_{m2}^a q_a + \frac{1}{2}\sum_{a,b} u_{m2}^{ab} q_a q_b & \cdots & V_m^0 + \sum_a u_{mm}^a q_a + \frac{1}{2}\sum_{a,b} u_{mm}^{ab} q_a q_b - \tilde{\mathrm{V}}(\boldsymbol{q}) & \cdots \\ \vdots & \vdots & & \vdots & \end{bmatrix} \begin{bmatrix} \mathrm{c}_1(\boldsymbol{q}) \\ \mathrm{c}_2(\boldsymbol{q}) \\ \vdots \\ \mathrm{c}_m(\boldsymbol{q}) \\ \vdots \end{bmatrix} = 0 \quad (10)$$

where

$$u_{ij}^a = \int \mathrm{d}\boldsymbol{r}\phi_i^{0*}(\boldsymbol{r})\left(\frac{\partial \mathrm{U}}{\partial q_a}\right)_0 \phi_j^0(\boldsymbol{r})$$
$$u_{ij}^{ab} = \int \mathrm{d}\boldsymbol{r}\phi_i^{0*}(\boldsymbol{r})\left(\frac{\partial^2 \mathrm{U}}{\partial q_a \partial q_b}\right)_0 \phi_j^0(\boldsymbol{r}) \quad (11)$$

The off-diagonal terms in the square matrix of eqn. (10) are called Herzberg-Teller (HT) coupling terms, and they mix the CBO basis functions, with nuclear-coordinate-dependent coefficients. This is identical to Herzberg's type (a) vibronic interaction (*18*). It leads to nuclear coordinate $\boldsymbol{q}$ dependence in the electronic wavefunctions. The nontrivial solution of eqn. (10) is obtained by setting the secular determinant to zero. The solutions are a set of electronic energies $\{\tilde{\mathrm{V}}_m(\boldsymbol{q})\}$ and a corresponding complete set of electronic wavefunctions $\{\tilde{\phi}_\mathrm{m}(\boldsymbol{r},\boldsymbol{q})\}$. Since we have included the Coulomb potential of the nuclei in $\mathrm{U}(\boldsymbol{r},\boldsymbol{q})$, the electronic energies $\{\tilde{\mathrm{V}}_m(\boldsymbol{q})\}$ in this case are the potential energy surfaces for the nuclear motion.

The complete set of electronic wavefunctions can be used as a basis set to determine the solutions to the approximate vibronic Hamiltonian,

$$[\mathrm{T}(\boldsymbol{q}) + \mathrm{T}(\boldsymbol{r}) + \tilde{\mathrm{U}}(\boldsymbol{r},\boldsymbol{q})]\tilde{\Psi}(\boldsymbol{r},\boldsymbol{q}) = E\tilde{\Psi}(\boldsymbol{r},\boldsymbol{q}) \quad (12)$$

This is done by expanding the vibronic wavefunction as,

$$\tilde{\Psi}(\boldsymbol{r},\boldsymbol{q}) = \sum_{m=1}^{\infty} \chi_m(\boldsymbol{q})\tilde{\phi}_m(\boldsymbol{r},\boldsymbol{q}) \quad (13)$$

The coefficients $\{\chi_m(\boldsymbol{q})\}$ in the expansion which are functions of the nuclear coordinate $\boldsymbol{q}$ are the vibrational wavefunctions. It is straightforward to obtain the coupled equations for the vibrational wavefunctions. The coupling arises from the nuclear kinetic energy operator. It is common to omit these so-called BO coupling terms. The vibrational wavefunctions then satisfy the following simple Schrodinger equation,

$$[\mathrm{T}(\boldsymbol{q}) + \tilde{\mathrm{V}}_m(\boldsymbol{q})]\chi_{mv}(\boldsymbol{q}) = E_{mv}\chi_{mv}(\boldsymbol{q}) \quad (14)$$

with $\tilde{\mathrm{V}}_m(\boldsymbol{q})$ as the potential energy term. The vibrational wavefunctions are labelled by an electronic quantum number m, and a vibrational quantum number v. In this approximation, the vibronic wavefunction takes the BO form,

$$\tilde{\Psi}_{mv}(\boldsymbol{r},\boldsymbol{q}) = \tilde{\phi}_m(\boldsymbol{r},\boldsymbol{q})\chi_{mv}(\boldsymbol{q}) \quad (15)$$

as simply a product of electronic and vibrational wavefunctions.

Special Case: Nondegenerate Electronic States

In this section, we shall look at the detailed solution of eqn. (10) for the simplest, special case where an *electronic state* m *is nondegenerate, and is well separated in energy from all other electronic states.*

Electronic Motion

In this case, it is justified to retain only the HT coupling terms that involve the electronic state m in eqn. (10),

$$\begin{bmatrix} V_1^0 + \sum_a u_{11}^a q_a + \frac{1}{2}\sum_{a,b} u_{11}^{ab} q_a q_b - \tilde{\mathrm{V}}(\mathbf{q}) & 0 & \cdots & \sum_a u_{1m}^a q_a + \frac{1}{2}\sum_{a,b} u_{1m}^{ab} q_a q_b & \cdots \\ 0 & V_2^0 + \sum_a u_{22}^a q_a + \frac{1}{2}\sum_{a,b} u_{22}^{ab} q_a q_b - \tilde{\mathrm{q}}(\boldsymbol{q}) & \cdots & \sum_a u_{2m}^a q_a + \frac{1}{2}\sum_{a,b} u_{2m}^{ab} q_a q_b & \cdots \\ \vdots & \vdots & \vdots & \vdots & \\ \sum_a u_{m1}^a q_a + \frac{1}{2}\sum_{a,b} u_{m1}^{ab} q_a q_b & \sum_a u_{m2}^a q_a + \frac{1}{2}\sum_{a,b} u_{m2}^{ab} q_a q_b & \cdots & V_m^0 + \sum_a u_{mm}^a q_a + \frac{1}{2}\sum_{a,b} u_{mm}^{ab} q_a q_b - \tilde{\mathrm{V}}(\boldsymbol{q}) & \cdots \\ \vdots & \vdots & & \vdots & \end{bmatrix} \begin{bmatrix} \mathrm{c}_1(\boldsymbol{q}) \\ \mathrm{c}_2(\boldsymbol{q}) \\ \vdots \\ \mathrm{c}_m(\boldsymbol{q}) \\ \vdots \end{bmatrix} = 0 \quad (16)$$

The solution of eqn. (16) is equivalent to the application of first-order perturbation theory to eqn. (7), and we obtain the m electronic state wavefunction and energy correct to quadratic terms in $\boldsymbol{q}$ to be,

$$\tilde{\phi}_m(\boldsymbol{r},\boldsymbol{q}) \simeq \phi_m^0(\boldsymbol{r}) + \sum_{j\neq m}^{\infty} \left\{ \frac{\sum_a^{3N-6} u_{jm}^a q_a + \frac{1}{2}\sum_{a,b}^{3N-6} u_{jm}^{ab} q_a q_b}{V_m^0 - V_j^0} \right\} \phi_j^0(\boldsymbol{r}) \quad (17)$$

and

$$\tilde{\mathrm{V}}_m(\boldsymbol{q}) \simeq V_m^0 + \sum_a^{3N-6} u_{mm}^a q_a + \sum_{a,b}^{3N-6} g_{mm}^{ab} q_a q_b \quad (18)$$

respectively, where

$$g_{mm}^{ab} = \frac{1}{2} u_{mm}^{ab} + \sum_{j\neq m}^{\infty} \frac{u_{mj}^a u_{jm}^b}{V_m^0 - V_j^0} \quad (19)$$

Potential Energy Surfaces

Since most processes occur from the ground potential energy surface, it is of interest to know how an isolated, nondegenerate excited m electronic state potential energy surface is oriented relative to it. The ground potential energy surface is in most cases nondegenerate and well separated from the other excited electronic states, and is given by eqn. (18) as,

$$\tilde{\mathrm{V}}_1(\boldsymbol{q}) = V_1^0 + \sum_a^{3N-6} u_{11}^a q_a + \sum_{a,b}^{3N-6} g_{11}^{ab} q_a q_b \quad (20)$$

We are free to define the zero of energy, and so we can set $V_1^0 = 0$. We can also choose $\boldsymbol{q} = 0$ to be the equilibrium configuration for the nuclei on the ground electronic state, in which case $u_{11}^a = 0$, $a = 1, 2, \ldots 3N - 6$. Thus eqn. (20) reduces to

$$\tilde{\mathrm{V}}_1(\boldsymbol{q}) = \sum_{a,b}^{3N-6} g_{11}^{ab} q_a q_b \quad (21)$$

By an orthogonal transformation—a rotation—the ground potential energy surface takes the diagonal form,

$$\tilde{\mathrm{V}}_1(\boldsymbol{q}) = \sum_a^{3N-6} h_a q_a^2 \quad (22)$$

where $\boldsymbol{q}$ now denotes the mass-weighted normal coordinates. This is a $3N - 6$ dimensional harmonic surface.

Any other isolated, nondegenerate electronic state m has a potential energy surface given by eqn. (18), where $\boldsymbol{q}$ now denotes the mass-weighted normal coordinates of the ground potential energy surface. Consider the coefficient u_{mm}^a for the linear term in $\boldsymbol{q}$. If q_a is a nontotally symmetric mode, then, since m is a nondegenerate electronic state, the direct product $\Gamma(\phi_m^0) \times \Gamma(q_a) \times \Gamma(\phi_m^0)$ does not contain the totally symmetric representation. Thus $u_{mm}^a = 0$ for a nontotally symmetric mode q_a. On the other hand, if q_a is a totally symmetric mode, the same direct product will be totally symmetric, and thus u_{mm}^a may not vanish. Next, for the coefficients $\{g_{mm}^{ab}\}$ of the quadratic terms in $\boldsymbol{q}$, we find by the same argument that g_{mm}^{ab} may not vanish if q_a and q_b belong to the same irreducible representation, $\Gamma(q_a) = \Gamma(q_b)$. Thus the excited m potential energy surface takes the simple form,

$$\tilde{\mathrm{V}}_m(\boldsymbol{q}) = V_m^0 + \sum_{\substack{a \\ \text{totally} \\ \text{symmetric}}} u_{mm}^a q_a + \sum_{\substack{a,b \\ \Gamma(q_a)=\Gamma(q_b)}} g_{mm}^{ab} q_a q_b \quad (23)$$

Comparing this with the ground potential energy surface eqn. (22), we can draw several conclusions about the isolated, excited, nondegenerate potential energy surfaces. For conciseness, we shall present them as theorems.

Theorem 1: The equilibrium configuration of the excited m potential energy surface can be *displaced* along the totally symmetric modes relative to the equilibrium configuration on the ground potential energy surface.

Proof: In eqn. (23), the potential energy can have a linear dependence on the totally symmetric coordinates q_a.

Theorem 2: If the harmonic approximation holds, the equilibrium configuration of the excited m potential energy surface is *undisplaced* along the nontotally symmetric modes relative to the equilibrium configuration on the ground potential energy surface.

Proof: In eqn. (23), the potential energy has no linear dependence on the nontotally symmetric coordinates q_a.

The harmonic approximation is not a necessary condition for the validity of Theorem 1. The potential energy surface along the totally symmetric mode could very well be a Morse potential, and Theorem 1 would still hold. Theorems 1 and 2 taken together physically state that the geometry of the molecule in an excited electronic state is of the same point group as in the ground electronic state if both these states are isolated and nondegenerate.

There can be cases where the harmonic approximation may not be a good description for the nontotally symmetric mode, and Theorem 2 becomes invalid. An example is a double-well potential with a local maximum, $U_{mm}^a = 0$ and $g_{mm}^{aa} < 0$, at q_a 0. The equilibrium position will then be located away from $q_a = 0$. If this happens for the excited state, say, then the geometry of the molecule in the excited electronic state will be different from the geometry in the ground electronic state which is located at $q_a = 0$. Such double-well potentials are well known for the totally symmetric bending vibrations, as in the ground state of NH_3 and the excited states of HCN and CS_2 (*19*). It is important to note that, in the case of an isolated, nondegenerate electronic state, symmetry allows double-well potentials for both nontotally symmetric stretching and bending vibrations. The case of the double-well potential for the nontotally symmetric stretch has so far been discussed only from the point of view of the pseudo Jahn-Teller effect (*20*), which involves two vibronically (HT) coupled nearby electronic states with harmonic potential energy surfaces.

Some possible forms and orientations of the potential energy surfaces along totally symmetric and nontotally symmetric modes are illustrated in Figure 1 for one dimension, and Figure 2 for two dimensions.

Theorem 3: The normal modes in the excited electronic state are simply displacements and rotations of the normal modes in the ground electronic state. The displacements occur along the totally symmetric modes; and the rotations are for normal modes belonging to the same irreducible representation.

Proof: The displacements along the totally symmetric modes are given by Theorem 1. We only need to show the rotations of the normal modes. Now, the matrix $[g_{mm}^{ab}]$, $a,b = 1,2,\ldots, 3N - 6$ in eqn. (23) is block diagonal, each block belongs to a single irreducible representation. Within each block, there may be quadratic cross terms between normal modes, and an orthogonal transformation—a rotation—will get it into the diagonal form, similar to eqn. (22) for the ground electronic state. This is known as the Duschinky rotation (*21–24*).

Theorem 4: If the equilibrium geometries of the molecule in the excited and the ground electronic states belong to different point groups, then Theorems 1, 2, and 3 will apply to those modes that transform in the same way under common symmetry elements of the two groups.

Proof: Such common normal modes can be given the same labels, and the theorems compare normal modes with the same labels in the nondegenerate ground and excited electronic states.

Illustrative Examples

The results obtained above have important implications for molecular spectroscopy. The potential energy surfaces contain information about the dynamics of the molecular framework. The dynamics have a direct bearing on the spectra. We shall confine ourselves to only electronic and Raman spectroscopies.

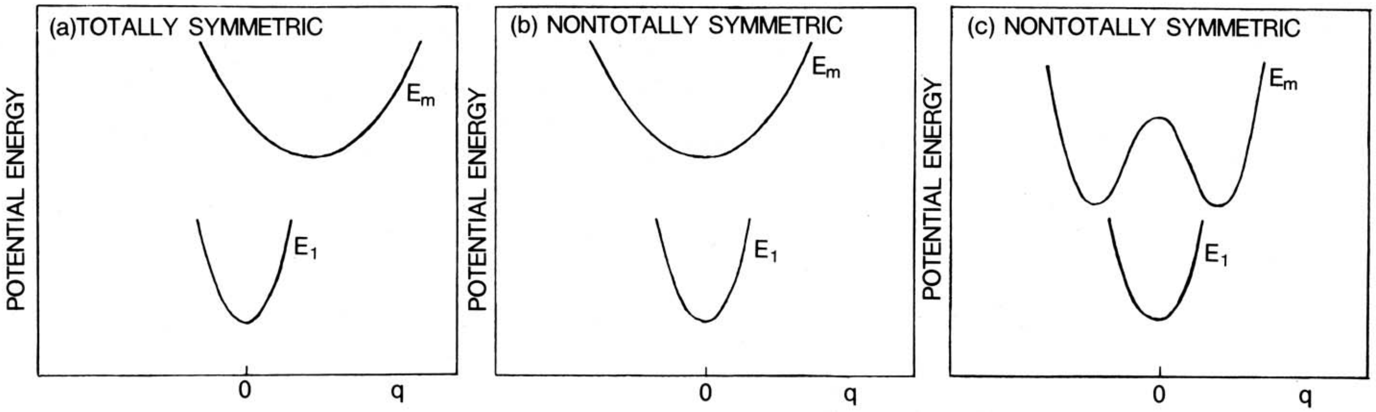

Figure 1. Contour plots of one-dimensional potential energy surfaces. (a) Displaced harmonic oscillators for the totally symmetric mode. (b) Undisplaced harmonic oscillators for the nontotally symmetric mode, and rarely for the totally symmetric mode. (c) Double well for the excited state potential energy surface of a nontotally symmetric mode.

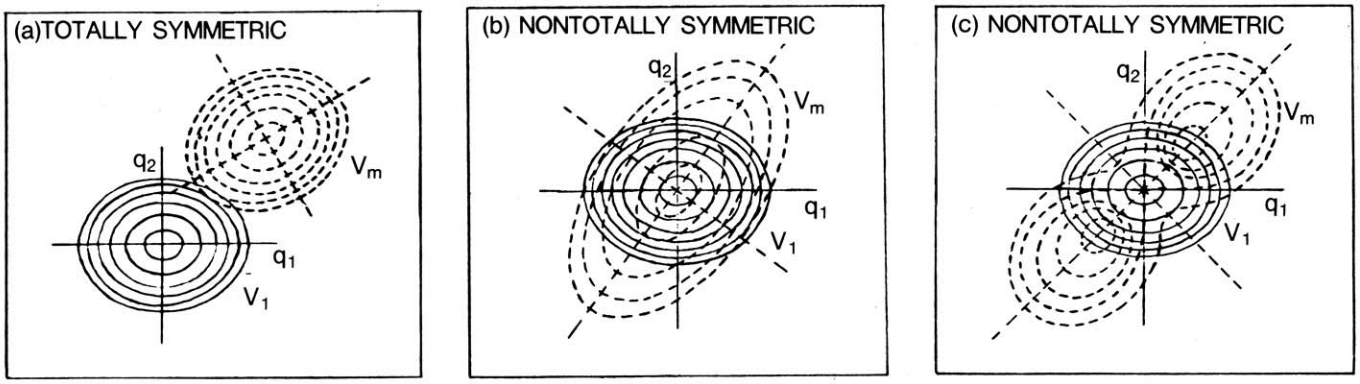

Figure 2. Contour plots of two-dimensional potential energy surfaces. (a) Displaced and rotated harmonic oscillators for the totally symmetric modes. (b) Undisplaced, but rotated, harmonic oscillators for the nontotally symmetric modes, and rarely for the totally symmetric modes. (c) Double well alone one mode in the excited state potential energy surface for nontotally symmetric modes. The modes in the excited state can be rotated relative to the modes on the ground state surface.

Electronic Spectroscopy

The intensity of an electronic transition is proportional to the square of the transition dipole moment $\boldsymbol{R}_{e'v'e''v''}$, where single prime labels the upper state, and double prime is for the lower state. The Born-Oppenheimer approximation enables us to factor the vibronic wavefunction into electronic and vibrational wavefunctions,

$$\Psi_{ev}(\boldsymbol{r},\boldsymbol{q}) = \phi_e(\boldsymbol{r},\boldsymbol{q})\chi_{ev}(\boldsymbol{q}) \tag{24}$$

The transition dipole moment is then given by,

$$\boldsymbol{R}_{e'v'e''v''} = \int d\boldsymbol{q}\,\chi^*_{e'v'}\chi_{e''v''}\{\int d\boldsymbol{r}\,\phi^*_{e'}\boldsymbol{M}\phi_{e''}\} \tag{25}$$

where $\boldsymbol{M} = \sum_i e\,\boldsymbol{r}_i$ is the electric dipole moment.

In the Condon approximation, CBO electronic wavefunctions are used in eqn. (25). The electronic part of the transition dipole moment,

$$\boldsymbol{R}^0_{e'e''} = \int d\boldsymbol{r}\,\phi^*_{e'}\boldsymbol{M}\phi_{e''} \tag{26}$$

is then a constant, and we have

$$\boldsymbol{R}_{e'v'e''v''} = \boldsymbol{R}^0_{e'e''}\int d\boldsymbol{q}\,\chi^*_{e'v'}\chi_{e''v''} \tag{27}$$

We define allowed electronic transitions as those for which $\boldsymbol{R}^0_{e'e''} \neq 0$. For simplicity, we shall restrict ourselves to such transitions. The intensity is then given by the overlap of vibrational wavefunctions in the excited and initial electronic states.

In the case of the totally symmetric mode, the potential energy surfaces in the excited and initial electronic states are displaced, as shown in Figure 1a. Thus, the overlap of the vibrational wavefunctions is clearly nonzero for all values of v' and v'', that is,

$$\Delta v = 0, \pm 1, \pm 2, \ldots \tag{28}$$

This can be observed as vibrational progressions, with intensities determined by the relative displacement of the two potential energy surfaces. In general, the observation of vibrational progressions implies that there is a change in the equilibrium geometry of the molecule in the transition. The converse, however, is not necessarily true, e.g., thermal averaging can remove the vibrational structures.

Water is bent (C_{2v}) in the ground $\tilde{X}$ electronic state, but linear ($D_{\infty h}$) in the excited $\tilde{B}$ electronic state. The $\tilde{B}$-$\tilde{X}$ transition is symmetry allowed, under the (lower symmetry) C_{2v} point group. The transition results in a large change in the bending angle. The totally symmetric bending mode is therefore excited in the $\tilde{B}$ state, because of the change in equilibrium geometry. This explains the long progressions in the bending vibrations with frequency $\nu_2' = 800\ \text{cm}^{-1}$ in the 1400–1200 Å absorption region (*25, 26*).

Another example is the Ã-X̃ transition of NH_2 (*27*), where the large changes in the bending angle and N-H bond length give rise to vibrational progressions in the totally symmetric ($\nu_1' = 3325$ cm^{-1}) stretch and ($\nu_2' = 633$ cm^{-1}) bend.

In the case of the nontotally symmetric mode, the potential energy surfaces of the initial and excited electronic states are both of even parity in this coordinate, as shown in Figure 1b and c. Clearly, in such a case, the vibrational overlap in eqn. (27) is nonzero only if the vibrational quantum number v changes by an even number, that is,

$$\Delta v = 0, \pm 2, \pm 4, \ldots \tag{29}$$

The transitions with $v = 0$ should be the most intense, because the vibrational wavefunctions involved are very similar. If, by chance, the frequency of the nontotally symmetric mode is the same in the two states, then orthogonality of the vibrational wavefunctions would restrict the vibrational selection rule to just $\Delta v = 0$.

The allowed Ã-X̃ transition of SO_2 spans the region 3400–2600 Å. In addition to the fairly long progressions in the totally symmetric stretch ($\nu_1' = 764$ cm^{-1}) bend ($\nu_2' = 317$ cm^{-1}), there are some weak bands which can be assigned to the asymmetric stretch ($\nu_3' = 813$ cm^{-1}) (*28,29*). In the X̃ state, $\nu_3'' = 1362$ cm^{-1}. The strong progressions correspond to the change of S-O bond length and bending angle in the transition. The weak bands involve a change ($\Delta v_3 = \pm 2, \pm 4$) in v_3.

Raman Spectroscopy

Raman scattering can be viewed either in the energy frame (*30, 31*) or the time frame (*10, 11*). The two viewpoints are equivalent. We shall use the less conventional, but physically picturesque, time-dependent viewpoint. In view of the importance of molecular dynamics, this is perhaps the most natural viewpoint. For simplicity, we shall assume that the Condon approximation applies, and confine ourselves to one dimension.

The Raman intensity is proportional to the square of the polarizability α, and is a nine-component tensor. In the time-frame viewpoint (*10, 11*), the vibrational matrix element of the polarizability for fundamental Raman scattering is given by,

$$\alpha_{10} = \sum_{e'} \boldsymbol{R}^0_{e''e'} \boldsymbol{R}^0_{e'e''} \left\{ \int_0^\infty \mathrm{d}t e^{i(E_{e''0} + \hbar\omega)t/\hbar} \langle \chi_{e''1} | \chi_{e''0}(t) \rangle \right. \\ \left. + \text{ nonresonant term} \right\} \tag{30}$$

This involves a sum over all excited e' states; and for each state there is a resonant term, which is given explicitly, and a generally much smaller nonresonant term. The difference in the two terms lies principally in the Fourier transform energy which, for the resonant term, is the sum of the initial vibronic energy $E_{e''0}$ and the energy of the incident light with frequency $\nu = \omega/2\pi$. The heart of the Raman effect is the vibrational overlap $\langle \chi_{e''1} | \chi_{e''0}(t) \rangle$, and the focus will be on how this overlap determines the Raman selection rules. The overlap depends on the form of the excited e' potential energy surfaces relative to the initial e'' potential energy surface. The wavefunction $\chi_{e''0}(q,t)$ arises from the propagation of the initial ground vibrational wavefunctions $\chi_{e''0}(q)$ on the excited e' potential energy surface. At each instant in time, we take the overlap of the propagated wavefunction with the (final) first excited vibrational state $\chi_{e''1}(q)$ of the fundamental Raman transition. For now, all we need to know is that the overlap must not be zero over the whole time interval in order to obtain some intensity in the Raman spectrum.

At time $t = 0$, $\chi_{e''0}(q,0)$ is orthogonal to $\chi_{e''1}(q)$, and the overlap is zero. Now, the excited e' potential energy surface is displaced along the totally symmetric coordinate q relative to the initial e'' potential energy surface, as shown in Figure 1. The wavepacket $\chi_{e''0}(q,0)$ will immediately begin to move on the excited e' potential energy surface, because of a resultant force, given by the gradient of the e' potential, acting on the wavepacket. This leads to a nonzero overlap $\langle \chi_{e''1} | \chi_{e''0}(t) \rangle$ for $t > 0$, and hence nonzero Raman intensity for the totally symmetric mode.

On the other hand, the even parity of the excited e' and initial e'' potential energy surfaces along the non-totally symmetric coordinate q, as shown in Figure 1b and c, implies that the initial even-parity wavefunction $\chi_{e''0}(q,0)$ will remain even-parity in q for all times t, when propagated on the e' potential energy surface. Hence, the overlap $\langle \chi_{e''1} | \chi_{e''0}(t) \rangle$ is identically zero for all times t, because the product $\chi_{e''1}\chi_{e''0}(t)$ is odd-parity in q. The Raman intensity is therefore zero for the nontotally symmetric mode.

We have just shown that the basis of the selection rules for Raman transition lies in the relative form of the excited e' and initial e'' potential energy surfaces. The almost universal phenomenological presentation of the Raman selection rules (*32–34*) in terms of the polarizability ellipsoids masks this important fact.

Recently, resonance Raman scattering (*35*) has generated a great deal of interest. Here again, the time-frame viewpoint coupled with a knowledge of the potential energy surfaces involved can account for most of the results. The beauty about the resonance Raman effect is that the theoretical description is very much simplified. The resonant excited e' state in eqn. (30) overwhelms all the other states. Only one, single resonant term corresponding to this resonant state determines the Raman intensity. This makes it possible to carry out the reverse process of deducing the excited e' potential energy surface from the Raman spectra (*36*).

As the incident light frequency is tuned closer to resonance with the excited e' state, the energy-time uncertainty principle implies that the wavepacket propagation (or relaxation of the nuclei) on the excited e' potential energy surface can proceed for a longer time interval. This increases the probability of a component in $\chi_{e''1}(q)$, thus giving an enhanced resonance Raman intensity. A good example is the totally symmetric 940 cm^{-1} umbrella mode of ammonia, where a tenfold resonance Raman enhancement has been observed (*37*) upon changing the incident light frequency from 5145 Å to 3511 Å. Ammonia is pyramidal in the ground X̃ state but is planar in the excited Ã electronic state. In the Ã electronic state, the initial wavefunction 0^+ (*38*) will move in the direction corresponding to the opening of the umbrella mode. The propagated wavepacket has nonzero overlap with the final 1^+ vibrational state, and hence it is an allowed "fundamental" Raman transition which can be resonance enhanced. It is useful to note that, because of the high barrier against inversion for ammonia in the ground X̃ electronic state, it is a very good approximation to consider just one half of the double well. The situation is then similar to Figure 1a. The 0^+ and 1^+ vibrational states resemble the ground and first excited vibrational states, respectively, on half the double well; and for this reason we label it as a "fundamental" Raman transition.

Conclusion

A systematic presentation of the Born-Oppenheimer approximation has been attempted. Some concepts—CBO basis set, HT coupling—in the BO lexicon were discussed. I stopped short of deriving the equations for the vibrational wavefunctions. The focus was on the potential energy surfaces for the special case of isolated, nondegenerate electronic states. There is scope for extension to degenerate or nearby electronic states. Some simple results for the form and orientation of the potential energy surfaces along the totally symmetric and nontotally symmetric modes were derived. Throughout the treatment, simple, but powerful, arguments from group theory, and matrix notation for conciseness have been used. Finally, the implications of the potential energy surfaces for electronic and Raman spectroscopies have been discussed. Numerous examples were quoted to illustrate the theory.

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