



Quantum consistent force field calculation of vibronic bandshapes and adiabatic potential energy surfaces for the 1Lb-1La electronic manifold of indole
by James Thomas Vivian

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry
Montana State University
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Abstract:

Vibronic bandshapes and adiabatic potential energy surfaces for the 1Lb(S1) and 1La (S2) electronic states of indole, are computed within the harmonic, Born-Oppenheimer, and Condon approximations by the Quantum Consistent Force Field (QCFF) semiempirical method. Franck-Condon factors are calculated utilizing the recursion relations of Doktorov, Malkin, and Man'ko which incorporate the effects of surface displacements, frequency shifts, and Duschinsky rotation and therefore provide FC factors which are exact within the harmonic approximation. In order to accurately calculate spectral bandshapes, the QCFF method has been modified to incorporate a difference-density scaling procedure based on the 260 nm band of benzene, and the scale factor is transferred directly to indole. Results for adiabatic potential surfaces for indole predict an avoided crossing of the Lb and La surfaces in the region of the La equilibrium molecular geometry. A semi-quantitative picture of the photophysics of the 1Lb-1La electronic manifold is developed in which the La state dynamics are interpreted in terms of a diabatic picture for the electronic potential energy surfaces. The diabatic potential surfaces are produced in an approximate way in which the configuration interaction eigenvectors are "frozen" at their values at the Ly equilibrium molecular geometry. The validity of the diabatic prescription is evidenced by the spectral bandwidth computed within the "frozen CI" method. A Landau-Zener curve crossing model is briefly explored in order to rationalize the absence of La fluorescence in jet-cooled indole.

**QUANTUM CONSISTENT FORCE FIELD CALCULATION
OF VIBRONIC BANDSHAPES AND ADIABATIC
POTENTIAL ENERGY SURFACES FOR THE $1L_b$ - $1L_a$
ELECTRONIC MANIFOLD OF INDOLE**

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James Thomas Vivian

A thesis submitted in partial fulfillment
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MONTANA STATE UNIVERSITY

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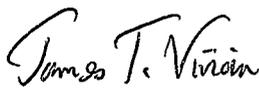
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In memory of Derek Hersey, climber extraordinaire and indoctrinated Fun Hog.

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ABSTRACT

Vibronic bandshapes and adiabatic potential energy surfaces for the 1L_b (S_1) and 1L_a (S_2) electronic states of indole, are computed within the harmonic, Born-Oppenheimer, and Condon approximations by the Quantum Consistent Force Field (QCFF) semiempirical method. Franck-Condon factors are calculated utilizing the recursion relations of Doktorov, Malkin, and Man'ko which incorporate the effects of surface displacements, frequency shifts, and Duschinsky rotation and therefore provide FC factors which are exact within the harmonic approximation. In order to accurately calculate spectral bandshapes, the QCFF method has been modified to incorporate a difference-density scaling procedure based on the 260 nm band of benzene, and the scale factor is transferred directly to indole. Results for adiabatic potential surfaces for indole predict an avoided crossing of the L_b and L_a surfaces in the region of the L_a equilibrium molecular geometry. A semi-quantitative picture of the photophysics of the 1L_b 1L_a electronic manifold is developed in which the L_a state dynamics are interpreted in terms of a diabatic picture for the electronic potential energy surfaces. The diabatic potential surfaces are produced in an approximate way in which the configuration interaction eigenvectors are "frozen" at their values at the L_b equilibrium molecular geometry. The validity of the diabatic prescription is evidenced by the spectral bandwidth computed within the "frozen CI" method. A Landau-Zener curve crossing model is briefly explored in order to rationalize the absence of L_a fluorescence in jet-cooled indole.

CHAPTER 1

INTRODUCTION

Indole Chromophore Photophysics

The indole chromophore is responsible for the low energy UV absorption near ~280 nm of the amino acid tryptophan. The absorption and emission for this band are relatively strong ($f \sim 10^{-1}$ - 10^{-2}) in both vapor and solution and the details of these photophysical processes depend very sensitively on the environment of the chromophore. For this reason, indole and tryptophan photophysics provide a unique and potentially powerful key towards the understanding of the structure, local environment, and dynamics within proteins.

One persistent problem in unraveling the details of the photophysics of indole is the existence of two quasi-degenerate electronic states which both contribute to the 280 nm absorption band. These states, the first two excited singlet states S_1 and S_2 , are labeled 1L_b and 1L_a , respectively (1), in gas phase, with the 1L_b being the lower of the two. It is believed that a detailed understanding of these two electronic states, which are responsible for ~90 percent of all protein UV absorption, is necessary in order to develop a knowledge and understanding of the much broader issue of protein structure and dynamics.

For these reasons, the indole chromophore has been the subject of intense experimental investigation (2-20), the focus of which relates to elucidation of the nature of the 1L_a and 1L_b electronic states and their photophysical behavior. Recently, polarized two-photon fluorescence excitation (PTPFE) experiments on jet-cooled indole (5,9), 3-methylindole (6,19), 5-methylindole (5), indole+water and indole+methanol van der Waals complexes (19,20) have helped to solidify existing assignments of L_b transitions in the gas phase absorption (excitation) spectrum of isolated indole. On the

other hand, the increased detail offered by jet-cooling techniques and polarization resolution has served to uncover new phenomena which have called into question previously existing experimental assignments and provided experimental features for which no suitable framework exists for their interpretation.

The most important and compelling example of this is in regard to the assignment of the L_a band origin for indole in both gas phase and solution experiments. While the L_b band origin is well established as occurring at $\sim 35,200 \text{ cm}^{-1}$ (284 nm), the L_a origin assignment remains an open question. At least two assignments have been proposed for the L_a origin, both of which raise considerable questions regarding the nature of the L_b - L_a electronic manifold. Strickland, et al. (18) performed vapor phase ($\sim 38^\circ\text{C}$) absorption of indole coupled with absorption experiments of indole in hexane and perfluorinated hexane solution and assigned the L_a band origin to $\sim 1450 \text{ cm}^{-1}$ (11) to the blue of the L_b origin on the basis of differential solvent-induced red shifts of the transitions observed for indole vapor.

In a beautiful series of experiments, Callis and co-workers (4-6,9) performed PTPFE in efforts to clearly identify the first L_a character transitions of indole. Their assignment, based on the different response of L_b and L_a transitions to circular and linearly polarized photons (one-color, two-photon polarization ratio), proposes a "split" L_a origin comprised of two fairly strong transitions observed at 455 and 480 cm^{-1} to the blue of the L_b band origin. The argument for this origin assignment hinges on the premise that these transitions are not simply L_b vibrations whose oscillator strength and intensity are derived from Herzberg-Teller vibronic coupling to the L_a state and thus behave as false origins, depending upon the nearness of the L_a state (5,6).

Whether the 455 and 480 cm^{-1} indole transitions are truly the L_a origin or Herzberg-Teller induced false origins one fact is perfectly clear: the two-photon polarization ratios for these transitions unambiguously display L_a character (5,6,9). The difficulty in the

present context is one which pervades all of the more recent, high resolution experiments on the indoles and that is a need for a better theoretical understanding of the L_b - L_a electronic manifold in order to provide a framework for interpretation of these experiments and to cast away the level of speculation which has previously been necessary to attempt to answer questions regarding the L_a origin.

From a theoretical perspective, indole presents considerable challenges and several unique problems which make it less than amenable to a comprehensive, accurate, and definitive treatment. First, the relative size of the molecule (16 atoms, 10 π electrons) makes ab-initio treatments difficult and computationally expensive (21-23,27), and there are a sufficiently large number of degrees of freedom (42 vibrational modes) to make a comprehensive treatment in terms of wavepacket dynamics (28-31) an unlikely prospect. Further, since most of the issues of interest are concerned with excited states, the demands and challenges to theory are amplified exponentially.

The central issue and desired goal should be a detailed knowledge of the electronic structure of the L_b and L_a excited states, since all desired properties follow from this. Although the picture of electronic structure will be, by necessity, only an approximate one, a suitable theory for indole photophysics is one in which the (approximate) electronic structure of these two states is sufficiently accurate to provide for the calculation of spectral bandshapes which are at least in qualitative (and at best, semi-quantitative) agreement with experiment.

To date, no calculations of the indole UV-absorption spectrum have been performed. While there have been reasonably accurate normal coordinate treatments, based on semi-empirical force fields (32,98), these treatments have been restricted to consideration of the ground state potential surface and therefore cannot be used reliably for bandshape calculations of UV-VIS spectra. Ab-initio treatments for indole have been performed as well (25-27), but these have been restricted either to the ground electronic state (25,26)

or are prohibitively expensive for excited states (27), thus making a normal-coordinate treatment within the ab-initio approach an impossibility.

The most comprehensive theoretical treatment of indole, to date, has been that of Callis (33), utilizing a spectroscopically calibrated semiempirical molecular orbital method. This method, which is a special spectroscopic parameterization of the intermediate neglect of differential overlap + configuration interaction method (INDO/S-CI), provides for the calculation of transition energies, oscillator strengths, polarizations, state dipoles, and two-photon properties, as well as bond orders, transition densities, and CI eigenvectors. Unfortunately, it does not predict excited-state equilibrium molecular geometries very accurately, nor is it possible to obtain normal modes of vibration from INDO/S-CI. Although this study does define a significant contribution in the theoretical domain and in many aspects a tour-de-force within the framework of INDO, it leaves open the need for spectral bandshape calculations for indole which are necessary at this stage to get a handle on the L_a origin questions which remain.

Further, it should be noted that in one very important respect the vibrational assignment of the L_a transitions is still in its infancy. Although a reasonably comprehensive vibrational assignment of L_b transitions is now available (12), the persisting uncertainty in the L_a origin identification makes impossible the assignment of individual L_a transitions, as evidenced by two-photon polarization ratios, to vibrations within the L_a electronic state. It is the purpose of this work to provide a theoretical picture of the spectroscopy of isolated indole and to attempt an explanation of the elusive L_a origin.

Statement of the Problem

This work will address the problems of calculation of vibronic bandshapes and potential energy surfaces for indole within the Born-Oppenheimer, harmonic, and

Condon approximations. At interest here is the clear identification of the existence of the L_a origin, examination of the possibility of Herzberg-Teller vibronic coupling of L_b vibrations to the L_a electronic state, and a detailed, quantitative picture of the L_b - L_a electronic manifold in terms of Born-Oppenheimer adiabatic potential energy surfaces.

We are interested here in the full potential energy surfaces, in addition to the minimum positions on the respective surfaces for the ground and first two excited singlet states of indole. The reason for this is that the full surfaces are required in order to identify possible avoided crossings of the L_b and L_a electronic states. While the avoided crossings can be identified, in principle, through examination of the nature of the eigenvectors for the excited state electronic wavefunctions, a more detailed picture is provided by the surfaces themselves.

In addition, we wish to establish from this work the magnitude of the interaction between the L_b and L_a electronic states. Although we carry out all calculations of potential energy surfaces within the Born-Oppenheimer adiabatic approximation, without nuclear kinetic energy coupling terms, we are nonetheless able to pose the following question: "Is the Born-Oppenheimer adiabatic picture sufficient to predict accurate spectral bandshapes for isolated indole or is the nature of the excited state potential surfaces better described in terms of a diabatic picture?"

Theoretical Approach

Our approach to the problems outlined above is to perform calculations of spectral bandshapes and potential energy surfaces within the framework of semiempirical molecular orbital theory. In terms of level of theory, the semiempirical approach is a reasonably modest one, representing a significant improvement over standard Hückel MO theory in that the resonance and Coulomb integrals are explicitly incorporated into the formalism, but remaining well outside the essentially "exact" (and computationally

expensive) prescription of ab-initio theories.

We have chosen to employ the Quantum Consistent Force Field (QCFF) method of Warshel, et al. (34-37) as the source of our semiempirical quantum chemical calculations. The reasons for this choice are multi-fold. In the first place, QCFF can be regarded on a theoretical level as essentially a Pariser-Parr-Pople (PPP) Hamiltonian which includes configuration interaction (CI) for singly excited configurations in order to provide excited state properties. A central feature to the QCFF method is the adaptation of empirically derived analytic forms for the core, Coulomb, and resonance integrals, and constitutes an approximate approach which is flexible and efficient enough to provide many of the quantum-mechanical properties of interest with reasonable accuracy and without the exhaustive computational efforts required by more high-end ab-initio theories.

A second and perhaps more attractive feature of QCFF is in regard to the form of the molecular potential energy surface, which is provided for all electronic states as an explicit function of the $3N$ -Cartesian coordinates of the nuclei comprising the molecule. This has considerable advantages over a representation in internal coordinates (which are provided as well by QCFF) both in terms of out-right convenience in dealing with the excited state potentials but in terms of the normal modes of vibration.

QCFF provides, in canonical form, for the calculation of molecular geometries, bond orders, total molecular energy, configuration interaction excitation energies, CI eigenvectors, transition dipoles, oscillator strengths, and normal modes of vibration (eigenvectors and frequencies). As such, QCFF is a particularly useful package in that it incorporates a great deal of the properties of interest into one convenient and reasonably efficient suite of codes.

In our work with QCFF, we have introduced several modifications to the routines in order to carry out the calculation of spectral bandshapes and potential surfaces. For the most part, these modifications are either trivial adjustments of the QCFF in terms of

procedure or extensions of existing calculations within the code. The overall integrity of the QCFF method has been preserved in terms of parameterization and the functional forms of the model potentials and empirical integrals employed. These modifications are documented in detail in the chapter on Computational Methods (Chapter Three) of this thesis. The modified version of QCFF is designated as QCFFBOZE in order to distinguish our version from the canonical form which is commonly in use.

QCFF thus provides the ingredients -- normal modes of vibration and excitation energies -- necessary for the calculation of spectral bandshapes and potential energy surfaces. The spectral bandshape calculations require the evaluation of Franck-Condon factors, which govern the relative transition intensities for the electronic states at the limit of zero Kelvin. The zero Kelvin "stick" spectrum FC factors have essentially no width -- they represent infinitely narrow resonances -- which is appropriate for identifying the frequencies and relative intensities of the center of the bands but is nonphysical since it fails to account even for the effects of lifetime (Heisenberg) broadening of the transitions. The broadening is handled phenomenologically in our calculations through the application of Gaussian broadening factors to the zero Kelvin "stick" transitions.

The formalism for the calculation of Franck-Condon factors is described in detail in Chapter Two, and details of the algorithm implemented for the evaluation of the FC overlap integrals are discussed in Chapter Three. It suffices here to state that we utilize the recursion relations of Doktorov, et al. (39,40), to carry out the evaluation of the FC factors. This method has the advantage of being exact within the harmonic approximation in that it incorporates the effects of normal coordinate displacements, frequency shifts, and Duschinsky rotation (41), in addition to being reasonably straightforward to implement.

Potential energy surface calculations are carried out in a straightforward manner within the QCFFBOZE framework. The exception to this is the development of a "frozen

configuration interaction" technique which ultimately provides a direct method to approximate the limit of diabatic potential energy surfaces. The implications of this frozen CI method for the calculated spectral bandshapes provides a particularly insightful piece of information regarding the L_a electronic state of indole and constitutes one of the more important results of this work.

Lastly, with regard to the underlying philosophy for the calculations undertaken in this work, our approach is first and foremost a semiempirical one throughout. Our overriding goal is to make connection with experiment rather than to develop new theoretical methods. The main thread throughout is one of flexibility, coupled with direct input from experimental data, in order to develop a comprehensive and accurate characterization of the L_b - L_a electronic manifold. To that end, we have endeavored to elevate the methods which were developed in the course of this work to a status which is not simply that of a fitting procedure. Noteworthy is the fact that we have not empirically adjusted the computed normal coordinate displacements and vibrational frequencies in order to fit spectral bandshapes to agree with experiments -- the only input from experiment at the level of the bandshape calculations is in the form of the spectral bandwidth, oscillator strength ratio for the L_b and L_a states, and the L_a origin energy displacement. In order to accomplish this, the introduction of a difference-density scaling factor was developed within the QCFF formalism (this is, in fact, the definitive feature of QCFFBOZE) in order to globally adjust the bond length changes upon electronic excitation and therefore adjust the normal coordinate displacements without having to appeal to the experimental relative intensities to accomplish this (except for benzene, the calibration molecule). The difference-density scaling method was developed such that QCFFBOZE is able to correctly predict the $B_{2u} \leftarrow A_{1g}$ (L_b) absorption spectrum for benzene. However, this method of difference-density scaling appears to have some transferability between molecules, since we apply directly to indole the scaling parameter

which was determined for benzene.

Despite the relatively modest level of theory employed in this work, we are able to obtain reasonably good results for indole in terms of computed spectral bandshapes and potential energy surfaces which strongly reflect what is observed in gas phase experiments. Modest it is: we utilize, through QCFFBOZE, only a CI singles description for the excited states, and all calculations are carried out at the harmonic level of approximation. Even the frozen CI method for approximating a diabatic description of the potential energy surfaces is remarkably simple in terms of approach but provides a very useful picture of the breakdown of the Born-Oppenheimer approximation without having to recast the molecular Hamiltonian to incorporate nuclear kinetic energy couplings. In these respects, the calculations described in this thesis met with considerable success and provide the theoretical framework which is necessary for understanding the interesting and challenging aspects of indole photophysics which have previously eluded explanation.

Thesis Outline

In this thesis it is demonstrated that a previously proposed avoided crossing of the L_b (S_1) and L_a (S_2) electronic surfaces based on the results of fluorescence excitation experiments on jet-cooled indole and methylindoles (5,6,9) is predicted at the CI singles level of semiempirical MO theory near the region of the L_a potential surface minimum. It is shown that an adequate description of the L_b - L_a electronic manifold in indole is provided by an effectively diabatic picture for these two states, and that breakdown of the Condon approximation in the region of the L_b - L_a avoided crossing region (ACR) is strongly evidenced. The picture which emerges in terms of calculated spectral bandshapes is that in which the diabatic prescription for the surfaces correctly predicts the L_a bandwidth and band maximum, providing strong evidence for curve-crossing by L_a

vibrations near the avoided crossing region.

The outline of this thesis is as follows. This Introduction chapter serves to briefly outline the relevant photophysical problems observed in indole and to provide a qualitative introduction to the theoretical techniques employed in this work, as well as to emphasize the problems at hand. Chapter Two, Theoretical Foundations, outlines in considerable detail the underlying assumptions, formalism, and concepts which provide the framework in which this work was carried out. In particular, the form of the Franck-Condon integral recursion relations is presented there, along with the jet-cooled versions of these expressions: Chapter Three, Computational Methods, focuses on the modifications to the QCFF method which were necessary to achieve accurate results for indole, as well as a detailed description of the difference-density scaling procedure which is unique to this work. Chapter Four, Results and Discussion, presents our preliminary results with QCFF for our test-case molecule, benzene, and the extension of the QCFFBOZE difference-density scaling procedure to indole. These results provide the basis for the Franck-Condon factors which are then utilized to examine the vibrational assignment of indole, for calculation of spectral bandshapes, and for the excited state potential energy surfaces. All results are presented and discussed in Chapter Four, along with a discussion which attempts to cast the results into the proper perspective in terms of experiment. In addition, a qualitative argument is presented to attempt to rationalize the experimental results for the methylindoles in light of the calculated results for isolated indole.

Finally, Chapter Five provides a summary and analysis of the collective results and presents a brief outline of suggestions for the logical extensions of the work contained in this thesis which appear promising. This outline or proposal for further work is provided in order to point out some of the areas in this study which appear to warrant further examination and to suggest potential improvements of the methods developed in this

work which could provide further insight into the details of the L_b - L_a electronic manifold of indole.

CHAPTER 2

THEORETICAL FOUNDATIONS

Molecular Hamiltonians and The Born-Oppenheimer Approximation

The Hamiltonian for a molecule comprised of N electrons and K nuclei can be written (in atomic units, $e = \hbar = m_e = 1$)

$$H = T_e + T_n + V_{ee} + V_{nn} + V_{en}$$

$$H = -\frac{1}{2} \sum_i^N \nabla_i^2 - \sum_\alpha^K \frac{1}{2M_\alpha} \nabla_\alpha^2 + \frac{1}{2} \sum_{i>j}^N \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} + \frac{1}{2} \sum_{\alpha>\beta}^K \frac{Z_\alpha Z_\beta}{|\mathbf{q}_\alpha - \mathbf{q}_\beta|} - \frac{1}{2} \sum_{i,\alpha}^{N,K} \frac{Z_\alpha}{|\mathbf{x}_i - \mathbf{q}_\alpha|}$$

where \mathbf{x} and \mathbf{q} denote electronic and nuclear coordinates, respectively, Z_α represents nuclear charge in multiples of the electron charge, and M_α represents nuclear mass in multiples of the electron mass. The first two terms in the Hamiltonian are the kinetic energy operators of the electrons (nuclei), the second two terms represent the potential energies of electron-electron (nuclear-nuclear) repulsion, and the last term is the electron-nuclear interaction.

The molecular Hamiltonian presented above is the exact electrostatic Hamiltonian in the sense that all of the forces involved are simple Coulomb interactions between particles and no approximations have been introduced except for neglect of spin-orbit (magnetic) coupling terms. The only attractive (i.e. negative) term in the Hamiltonian is the electron-nuclear interaction term, V_{en} . Further, it is important to note that this term is the only coupling term in that it involves both electronic and nuclear coordinates, and is thus the binding potential for the molecule. The presence of this term in the molecular Hamiltonian complicates the solution of the Schrödinger equation since it makes it impossible to express the Hamiltonian as a simple sum of an electronic Hamiltonian and a nuclear Hamiltonian. In this sense, the coupling term is the crux t

term of the Hamiltonian since it makes rigorous separation of electronic and nuclear degrees of freedom an impossibility.

If we rewrite the molecular Hamiltonian by grouping terms involving electronic and nuclear coordinates, we obtain

$$H = [T_e(\mathbf{x}) + V_{ee}(\mathbf{x}) + V_{en}(\mathbf{x},\mathbf{q})] + [T_n(\mathbf{q}) + V_{nn}(\mathbf{q})].$$

It is worthwhile to consider the above Hamiltonian on physical grounds. First, electrons are much lighter (by at least a factor of 1836) than nuclei, and our intuition suggests that the electronic motion is much faster than the nuclear motion. Thus, to a very good approximation, the electrons can adjust "instantaneously" to the relatively slow motion of the nuclei. Within this level of approximation, we can approach the above Hamiltonian by treating the nuclear framework as being "clamped" in a particular configuration (specified by fixed nuclear coordinates, \mathbf{q}) and solving the Schrödinger equation for that molecular geometry. This procedure is repeated over several molecular geometries to obtain the total molecular energy as a function of nuclear coordinates.

This separation of electronic and nuclear motions is, in fact, the physical basis for the celebrated Born-Oppenheimer Approximation (42). The original paper by M. Born and R. Oppenheimer was based on time-independent perturbation theory in which a perturbation parameter involving the ratio of electronic to nuclear masses was introduced to treat the nuclear kinetic energy as a perturbation on a zeroth-order Hamiltonian equal to the sum of the electron kinetic energy and the total Coulomb energy. It is possible, however, to pursue the Born-Oppenheimer Approximation on well-motivated physical grounds without having to employ the methods of perturbation theory. In some sense, this approach consists of a Ansatz in which the Born-

Oppenheimer first-order perturbation expansion wavefunction is chosen as the correct wavefunction for the molecular Hamiltonian. In fact, this line of development has now become standard (43,47,84) and has relegated the original derivation by Born and Oppenheimer to the status of culture. The advantage of avoiding the language of perturbation theory, as will be demonstrated below, is that the concept of potential energy surfaces for the nuclear motion arises immediately in the development. Further, the development has a much more intuitive physical appeal which is not exhibited by perturbation-theoretic arguments.

We begin the development by treating the separation of time scales for nuclear and electronic motions. Formally, this procedure corresponds to treating the nuclear coordinate dependence of the Hamiltonian as a parameter. For a given molecular geometry, \mathbf{q}^* , the parametric Hamiltonian can be written

$$H(\mathbf{x}; \mathbf{q}^*) = [T_e(\mathbf{x}) + V_{ee}(\mathbf{x}) + V_{en}(\mathbf{x}; \mathbf{q}^*)] + [T_n(\mathbf{q}^*) + V_{nn}(\mathbf{q}^*)]$$

which represents a function of the electronic coordinates with the nuclei clamped at the geometry specified by \mathbf{q}^* . In this case, then, the parametric Hamiltonian does exhibit an effective separation in terms of electronic and nuclear degrees of freedom. Corresponding to this Hamiltonian we can construct an appropriate molecular wavefunction (with the same parametric dependence on nuclear coordinates as the Hamiltonian) as a product of separate electronic and nuclear wavefunctions

$$\Psi_{\text{BO}} = \psi_{\zeta}(\mathbf{x}, \mathbf{q}) \chi_{\zeta}^{\eta}(\mathbf{q})$$

where the subscript "BO" is to remind us that we are invoking the Born-Oppenheimer separation. The first term represents an eigenfunction of the terms involving electronic

coordinates at the specified nuclear coordinates. The second term involves only the nuclear coordinates and represents the wavefunction which describes the nuclear motion. Following this Ansatz through we write the time-independent Schrödinger equation in terms of the separated electron-nuclear wavefunction and evaluate the effect of the operators to obtain (after some rearrangement);

$$\begin{aligned} H\Psi_{B-O} &= \Psi_{\zeta} \left[\frac{-1}{2M} \frac{\partial^2}{\partial q^2} + V_{nn} + \epsilon_{\zeta} \right] \chi_{\zeta}^{\eta} + \left(\frac{-1}{2M} \right) \left[2 \frac{\partial \Psi}{\partial q} \frac{\partial \chi}{\partial q} + \chi_{\zeta}^{\eta} \frac{\partial^2 \Psi}{\partial q^2} \right] \\ &= E_{\zeta, \eta} \Psi_{\zeta} \chi_{\zeta}^{\eta} + \left(\frac{-1}{2M} \right) \left[2 \frac{\partial \Psi_{\zeta}}{\partial q} \frac{\partial \chi_{\zeta}^{\eta}}{\partial q} + \chi_{\zeta}^{\eta} \frac{\partial^2 \Psi_{\zeta}}{\partial q^2} \right] \end{aligned}$$

and in which the term $\epsilon_{\zeta, \eta}$ is identified as the electronic energy for a given nuclear configuration, \mathbf{q} . The subscripts, ζ and η , denote the electronic state and vibrational level, respectively. The latter terms in this expression involve, respectively, the slopes of the electronic and nuclear wavefunctions with respect to nuclear coordinates, and the curvature of the electronic wavefunction w.r.t. nuclear coordinates. It is the dependence of the electronic wavefunction on nuclear coordinates which is important here. These terms are, of course, a direct consequence of the coupling term -- they represent nuclear kinetic energy coupling.

In view of the expressions above, it is instructive to evaluate the matrix elements corresponding to the Hamiltonian. Proceeding in the usual manner, we obtain

$$\begin{aligned} \left\langle \zeta' n' | H | \zeta n \right\rangle &= \int dx \int dq \Psi_{\zeta'}^* \chi_{n'}^* H \Psi_{\zeta} \chi_n \\ &= E_{\zeta n} \delta_{\zeta \zeta'} \delta_{n n'} + \left(-\frac{1}{2M} \right) \int dx \int dq \Psi_{\zeta'}^* \chi_{n'}^* H \Psi_{\zeta} \chi_n \left\{ 2 \frac{\partial \Psi}{\partial q} \frac{\partial \chi}{\partial q} + \chi \frac{\partial^2 \Psi}{\partial q^2} \right\} \end{aligned}$$

Thus, the nuclear kinetic energy coupling terms do not vanish upon integration over electronic and nuclear coordinates, in general, and make some contribution to the

expectation value of the energy. These terms are referred to as "non-adiabatic" terms. Nonetheless, these terms are likely to be small relative to the electronic energy term, $E_{\zeta\eta}$, and can be neglected to a first approximation. In fact, it is precisely the neglect of these terms which define the form of the potential energy surface(s) for nuclear motion in the standard Born-Oppenheimer Approximation. For this reason, the Born-Oppenheimer Approximation is more correctly termed the "Adiabatic Born-Oppenheimer Approximation", and the resulting potential energy surfaces are referred to as "adiabatic potential energy surfaces".

Classical Treatment of Molecular Vibrations

The previous development provides formal expressions for the electronic potential energy surfaces through an effective separation of electronic and nuclear motions. In principle, then, the construction of the potential surfaces proceeds via solution of the separate Schrödinger equations for vibrational (nuclear) and electronic wavefunctions. The former problem can be handled to a very good approximation by the application of a classical model which describes the nuclear motions and leads to quantum mechanical wavefunctions for a familiar, elementary soluble problem: the simple harmonic oscillator. The electronic problem, on the other hand, is somewhat more complicated and requires a fully quantum-mechanical treatment for its solution. We focus here on the solution for the vibrational wavefunctions. The calculation of the electronic wavefunctions is described in detail in a later section.

We begin by envisioning a molecule in terms of a classical model in which the atoms are treated as point masses and the bonds are regarded as springs. We will not be concerned with the details of the electronic structure of the molecule at this point, but instead will focus simply on the classical mechanics of this simplified model.

For N atoms, we require $3N$ Cartesian coordinates to specify the location of all the

particles. If we then define x_i as the Cartesian displacement from equilibrium for atom "i", we can specify an arbitrary distortion of the molecule by $3N$ displacement coordinates. For small displacements from equilibrium, we can expand the potential energy in terms of the displacement coordinates as

$$V(\mathbf{x}) = V(\mathbf{x}^{(0)}) + \mathbf{F} \cdot \mathbf{x} + (1/2) \mathbf{x}^T \mathbf{K} \mathbf{x} + (\text{higher-order terms})\dots$$

where \mathbf{F} and \mathbf{K} are the matrices of first and second derivatives, respectively, of the potential. We require that the net force vanish at the equilibrium configuration, so the first derivative terms are zero. Also, we are interested only in the change in energy with respect to the equilibrium configuration, so we may therefore define the term $V(\mathbf{x}^{(0)})$ as zero and gauge the potential energy with respect to this reference. Since we are interested in infinitesimally small displacements from equilibrium, we can neglect the higher order terms in the expansion and obtain for the (approximate) potential energy of vibrational distortion

$$V(\mathbf{x}) = (1/2) \mathbf{x}^T \mathbf{K} \mathbf{x} .$$

This expression has a very simple physical interpretation: it is just Hooke's Law for a system of masses connected by springs. The coefficients, k_{ij} , are the force constants associated with the springs and represent the restoring force which tends to pull the masses back to their equilibrium positions. Note that this expression exhibits a quadratic dependence of the potential on the displacements, i.e. a harmonic potential. The higher-order terms, which have been neglected, are the so-called anharmonic contributions to the potential. These terms, when included, result in potential wells which are not parabolic.

Now that the form of the potential has been specified, it is possible to write down the equations of motion for the system. If we assume the springs are frictionless the system is conservative and the force is completely specified by the gradient of the potential. Therefore, we can immediately write the equation of motion for the i -th particle from Newton's Second Law as

$$m_i (d^2x_i/dt^2) = F_i = -(\partial V/\partial x_i) = -\sum_j k_{ij} x_j.$$

This represents a system of $3N$ simultaneous, second-order differential equations which must be solved to obtain the motion for each particle. We can solve this immediately by noting that the solution must be a function of time such that the second derivative of the function is proportional to the function itself. We are free to choose the solution to be of the form

$$x_i(t) = a_i \cos(\omega t + \phi)$$

which can be shown to have the desired property by direct substitution;

$$d^2x_i/dt^2 = -a_i \omega^2 \cos(\omega t + \phi).$$

Inserting this solution into the above set of coupled equations of motion yields

$$-m_i a_i \omega^2 \cos(\omega t + \phi) = -\sum_j k_{ij} a_j \cos(\omega t + \phi)$$

or more simply

$$-m_i a_i \omega^2 = -\sum_j k_{ij} a_j$$

which represents a set of $3N$ coupled, linear, homogeneous equations in the amplitudes, a_i , which must be solved to obtain the motion for the system. This last expression represents the secular equation which must be solved in order to obtain the vibrational frequencies for the system. In principle as well as in practice this is essentially a trivial problem in that all we are required to do is perform a reasonably simple matrix diagonalization.

On the other hand, we really do not need to carry out the diagonalization to know the

structure of the solution. We have already specified an oscillatory solution for the time dependence of the coordinates. That is, physically, all the masses (atoms) oscillating about their equilibrium positions with the same frequency and phase relationship. Thus, all the atoms move through their equilibrium positions at the same time, reach their classical turning points at the same time, and then reverse the motion. The phase for the motions is of no interest, and so may be arbitrarily set to zero. In fact, the only details of the solution that we do not know are the exact frequency of the motion and the absolute amplitudes of the motion. It turns out, however, that such a system of equations cannot produce a unique set of amplitudes (44,50). Rather, the closest we can obtain to a mathematically complete solution is the relative amplitudes.

Returning to the secular equations obtained previously, we can express this set of $3N$ simultaneous equations more compactly in matrix-vector notation as

$$\mathbf{K}\mathbf{a} = \omega^2 \mathbf{m}\mathbf{a}$$

where \mathbf{m} represents a diagonal mass matrix. Formally, this expression has the appearance of an eigenvalue equation except for the presence of the mass terms, i.e. each amplitude is multiplied by a different mass. We can convert this expression into an eigenvalue equation by transforming to mass-weighted form in the following manner;

- (i) replace each a_i by $m_i^{1/2} a_i$ and divide the i -th column of the \mathbf{K} -matrix by $m_i^{1/2}$, and
- (ii) divide the i -th row of the \mathbf{K} -matrix by $m_i^{1/2}$. Denoting the transformed \mathbf{K} -matrix by

\mathbf{U} , and the transformed amplitude vector by \mathbf{L} , we now have

$$\mathbf{U}\mathbf{L}_k = \omega_k^2 \mathbf{L}_k \quad (k = 1 \text{ to } 3N)$$

which is in the form of an eigenvalue equation. We denote the mass-scaled amplitude components as $L_{ik} = m_i^{1/2} a_{ik}$. In the language of eigenvalue problems the ω_k are the eigenvalues and the \mathbf{L}_k are the eigenvectors.

The procedure of mass-adjusting described above may seem awkward and ill-motivated at first sight. Nonetheless, it does serve to transform the secular equation into

an eigenvalue equation. It turns out, in fact, that the same eigenvalue problem will result automatically if we define at the beginning a set of mass-scaled displacement coordinates, $m_i^{1/2} x_i$, and derive the equations of motion in terms of them. Formally and physically, the results obtained are identical.

The advantage of being able to define an eigenvalue problem via mass-scaled displacement coordinates is that eigenvalue problems are tractable. In matrix language, the solution requires a similarity transformation, which is easy to perform. If we define \mathbf{L} (without the subscript, k) as the square matrix in which the eigenvectors (\mathbf{L}_k) are the columns, and ω the diagonal matrix of eigenvalues ω_k^2 , we have

$$\mathbf{U}\mathbf{L} = \omega \mathbf{L}$$

which can be diagonalized directly by the similarity transform

$$\mathbf{L}^{-1}\mathbf{U}\mathbf{L} = \mathbf{L}^{-1}\omega \mathbf{L} = \omega \mathbf{L}^{-1}\mathbf{L} = \omega$$

and we can take advantage of the fact that \mathbf{L} is an orthogonal matrix to obtain

$$\mathbf{L}^T\mathbf{U}\mathbf{L} = \omega,$$

where the "T" superscript denotes the transpose operation.

Transformation to Normal Coordinates

Recall the original expression for the potential energy change for vibrational distortion in terms of Cartesian displacement coordinates;

$$V(\mathbf{x}) = (1/2) \mathbf{x}^T \mathbf{K} \mathbf{x}.$$

If we now mass-scale the displacement coordinates and the force constants according to the prescription of the previous section, we obtain

$$V(\mathbf{q}) = (1/2) \mathbf{q}^T \mathbf{U} \mathbf{q}$$

where $q_i = m_i^{1/2} x_i$ and $U_{ij} = K_{ij} / (m_i^{1/2} m_j^{1/2})$.

If we now insert the identity $\mathbf{L}\mathbf{L}^T = \mathbf{1}$ before and after \mathbf{U} in the potential energy expression we can effectively diagonalize the (mass-adjusted) matrix of force constants t

to obtain

$$V(\mathbf{q}) = (1/2) \mathbf{q}^T \mathbf{L} \mathbf{L}^T \mathbf{U} \mathbf{L} \mathbf{L}^T \mathbf{q} = (1/2) \mathbf{Q}^T \boldsymbol{\omega}^2 \mathbf{Q} = (1/2) \sum_k \omega_k^2 Q_k^2$$

where we have defined

$$\mathbf{Q} = \mathbf{L}^T \mathbf{q}; \quad Q_k = \sum_i L_{ik} q_i.$$

The important point regarding the above transformation of the potential energy is that by recasting the change in energy for infinitesimal displacements in terms of the new coordinates, \mathbf{Q} , we obtain a simplified energy expression in which there are no cross terms between coordinates. The new coordinates, termed normal coordinates (due to the orthogonality of the eigenvectors, \mathbf{L}), therefore provide a separable energy expression which can be identified as a sum of individual quadratic terms for each mode of vibration. Therefore, in principle, we have completely solved the classical mechanics of molecular vibration: by diagonalizing the matrix of mass-adjusted force constants in a basis of mass-weighted Cartesian displacement coordinates, we generate the normal modes of vibration.

Quantum Mechanical Consequences

The previous result shows that we can express the potential energy for molecular vibration as a sum of independent harmonic oscillators. This result is based on a model in which the molecule is treated classically, as point masses connected by springs. Nonetheless, an energy expression which is a simple summation implies a separable quantum mechanical wavefunction which is a product of individual wavefunctions. Therefore, by construction, we can write the total vibrational wavefunction for this model as the product of $3N$ separate harmonic oscillator wavefunctions, one for each normal coordinate. This vibrational wavefunction will be valid to the extent that the approximation of small displacements is valid.

In this sense, we do not require a solution of the vibrational Schrödinger equation. If

we adopt normal coordinates as an approximation to describe the vibrational problem, the vibrational wavefunctions are essentially solved since they are simply harmonic oscillator wavefunctions. An advantage of using a harmonic description of the vibrations, when possible, is that much of the phenomenon involving harmonic oscillators is mathematically tractable (e.g. matrix elements) in closed form. In addition, even for situations where there are anharmonic effects, many of the essential features of the problem will be captured by a zeroth-order description in terms of harmonic oscillators, therefore giving such an approximate description a very satisfying physical appeal. For these reasons, calculations carried out within the harmonic approximation are well justified: in the event that a harmonic calculation does not agree with experiment, we gain the understanding that the phenomenon is anharmonic in character and some quantitative understanding of the degree of anharmonicity.

Semiempirical Molecular Orbital Theory

LCAO-MO-SCF Calculations

Although the Born-Oppenheimer approximation, in conjunction with the adaptation of a normal coordinate description of the vibrational modes, effectively solves the vibrational part of the problem, the electronic Schrödinger equation presents a unique computational problem. Much of the difficulty is due to the presence of electron-electron repulsion terms in the Hamiltonian, which makes impossible the decoupling of the electronic Schrödinger equation into separate one-electron equations. Further, the calculation of quantum mechanical expectation values requires the evaluation of an extremely large number of integrals, thus making the calculation of molecular properties a computationally expensive process. For these reasons, it is necessary to introduce approximations to make the solution of the electronic structure problem a tractable one.

