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A GAUGE THEORETIC TREATMENT OF ROVIBRATIONAL MOTION IN DIATOMS

by

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ABSTRACT

The Born-Oppenheimer approximation has long been the standard approach to solving the Schrödinger equation for diatomic molecules. In it nuclear and electronic motions are separated into “slow” and “fast” degrees of freedom and couplings between the two are ignored. The neglect of non-adiabatic couplings leads to an incomplete description of diatomic motion and in a more refined approach non-adiabatic couplings are uncoupled by transforming the angular momentum of the molecule and electrons into the body-fixed frame.

In this thesis we examine a “modern” form of the Born-Oppenheimer approximation by exploiting a gauge theoretic approach in a description of molecular motion. This procedure is described by a U(1) gauge field theory which we call the gauge covariant Born-Oppenheimer approximation. Using this approach we show that the non-adiabatic coupling terms are reproduced and manifest as an effective “magnetic monopole” vector potential that gives rise to an effective Lorentz type force.

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Chapter 1

INTRODUCTION AND OUTLINE

Because the quantum mechanical few body problem is intractable, the Born-Oppenheimer (BO) approximation [8] is a starting point for most molecular structure calculations. In the standard theory, the nuclear motion of diatoms are decoupled from that of the electronic, or fast, degrees of freedom but in a more refined treatment, non-adiabatic effects due to rotational motion are also included. Expressing the Hamiltonian for the electronic degrees of freedom in a body-fixed coordinate frame, and representing the total angular momentum of the molecule in that frame, non-adiabatic couplings that determine the rovibrational structure of the molecule are incorporated. That procedure is a cornerstone of molecular structure theory and was firmly established by the early days in the development of the wave mechanics.

In the 1980's a modern approach incorporating gauge theory ideas where introduced in the treatment of diatom rovibrational motion. In this thesis we explore the relationship between the standard approach and that using gauge theoretic techniques [37, 61].

In the conventional Born-Oppenheimer approximation the electronic and nuclear motion are taken to be uncoupled. The uncoupling procedure is justified by the assumption, because of the disparity between nuclear and electronic mass, that the nuclei adjust adiabatically to the motion of the electrons. In that picture, the electrons respond to the instantaneous position of the nuclei [8, 22] and one proceeds to calculate for the electronic wave functions at each value of inter-nuclear separation. In this description, electrons create a scalar potential field for a given nuclear configuration that back-reacts on the nuclei. This potential is called the Born-Oppenheimer potential and gives rise to the Feynman-Hellman force [24].

In a more complete treatment of this problem, the coupling between nuclear and electronic motion is no longer neglected [17]. Terms in the nuclear Hamiltonian induced by these couplings, typically called non-adiabatic couplings, modify the rotational eigenvalues and Born-Oppenheimer energies. Inclusion of non-adiabatic couplings, due to molecular rotation, lead to an effective nuclear Hamiltonian that is similar to that of the rotating symmetric top [34]. For a symmetric top, the eigenvalues of the rotational Hamiltonian are related to the Wigner d-functions [21], and for low energies the radial motion of the molecule can be accurately approximated by the eigenstates of a simple harmonic oscillator.

The gauge theoretic approach for the description of bound diatoms was first advanced by Moody, Shapere, and Wilczek [37] in 1986. They showed that the Hamiltonian governing nuclear motion in a diatom can be expressed as that of free rotator being acted upon by an effective gauge vector potential. In this description, the effective gauge potential was shown to be that produced by an effective "magnetic monopole" [37, 61, 64]. Using this approach, the rotational spectra of diatoms can be re-produced [37, 61] and it offers an alternative paradigm for molecular structure theory. Whereas both the standard theory and the gauge theoretic approach, which in this thesis we call the modern Born-Oppenheimer approximation, lead to identical ro-vibrational eigenvalues, the latter theory has significant advantages which we will elaborate on in this thesis. For example, the modern approach allows a better understanding for the mechanism in which total angular momentum (nuclear + electronic) is conserved in the BO approximation. In this theory the standard Hund's rules for angular momentum coupling is replaced by a mechanism in which the orbital angular momentum of the nuclei are coupled to the intrinsic angular momentum of the effective magnetic monopole [29, 37, 61] gauge field. Magnetic monopoles were first postulated by Poincaré [42], however the first quantum mechanical treatment of them was made in Dirac's seminal 1931 paper [18]. Whereas the latter are typically considered fundamental monopoles, i.e. arising from an extension of Maxwell's theory, the monopoles in molecular theory are effective ones that emerge as a consequence of the adiabatic approximation. The gauge theoretic approach also allows one to make connections with similar phenomena that occur in other areas of physics, including quantum Hall physics and the appearance of anyons in complex quantum systems. The gauge theory framework allows for a generalization of the Hellmann-Feynman force which plays an important role in molecular dynamics simulations. These forces arise from an effective scalar potential that describes the mean field induced by the fast degrees of freedom, i.e. electrons. In the modern Born-Oppenheimer approximation the vector potential leads to the appearance of effective Lorentz forces in addition to the traditional Hellmann-Feynman force.

We provide a brief outline of this thesis, which has two components, below. In the first part we review the traditional approach first advanced by Van Vleck, Kronig and others, of rovibrational molecular structure theory. We then introduce the modern approach and compare and relate the latter with the former. We make some suggestion for future investigations.

In Chapter 2 we review the traditional description of BO theory. Restricting the discussion to homonuclear systems, we express the Hamiltonian in a molecular coordinate system and review the BO separation of fast and slow degrees of freedom. In Chapter 3 we include the effects of non-adiabatic couplings in the Hamiltonian for the diatom. In chapter 4 we separate the angular and vibrational degrees of freedom, and show how inclusion of angular non-adiabatic couplings leads to an effective Hamiltonian that is identical to that of a symmetric top. The eigensolutions of the latter are obtained, and we illustrate how the rovibrational structure of bound diatoms are modified by the inclusion of rotational non-adiabatic couplings. In section 4.3 we review the treatment of vibrational motion, and obtain analytic results by approximating the BO eigenenergy with a Morse potential.

Chapter 5 introduces the second component of the thesis, in which we re-discuss the material introduced in the previous chapters from a gauge theory point of view. We first give an overview of general concepts, such as the notion of minimal coupling of a gauge field in the non-relativistic Schrodinger equation, gauge transformations and gauge invariance. In Chapter 7 we review the general quantum mechanical theory of magnetic monopoles. In section 7.1 we discuss the classic Dirac monopole, and in section 7.2 we show how mathematical inconsistencies in the latter can be resolved by employing a procedure introduced by T.T. Wu and C. N. Yang. We also discuss the concept of a non-integrable phase factor in quantum mechanics. The latter was introduced by Dirac in order to provide a deeper understanding of the nature and appearance of gauge fields in quantum mechanics. In the same paper in which Dirac introduced the idea of a non-integrable phase factor, he solved the quantum mechanical problem of a charged particle, an electron, interacting with a magnetic monopole. The Dirac-Maxwell monopole is a theoretical construct and searches in nature have so far been unsuccessful. Nevertheless the concept of the magnetic monopole plays an important part in modern theoretical physics, and we show in this thesis how effective, but not fundamental, magnetic monopoles do arise in molecular physics. In Chapter 8 we show how non-adiabatic effects in the Modern Born-Oppenheimer approximation manifest as the appearance of a gauge vector potential that describes a magnetic monopole. We show how the angular momentum of the rotating nuclei are coupled with the angular momentum contained in the static gauge field. The latter is shown to give rise to rovibrational structure identical to that derived in the classic theory of Van Vleck, Rabi and Kronig. We show how the induced gauge field gives rise to an effective, velocity-dependent, Lorentz force. We speculate on the applicability of the gauge theoretic approach in a more general context, and conclude with a summary of the thesis.

Chapter 2

TRADITIONAL QUANTUM DESCRIPTION OF DIATOMIC MOTION

The time-independent Schrödinger equation for a diatomic molecule is given by

$$H' \, \psi(\boldsymbol{R}, \boldsymbol{x}) = E' \, \psi(\boldsymbol{R}, \boldsymbol{x}) \tag{2.1}$$

where the wavefunction describing molecular motion is represented by $\psi(\boldsymbol{R}, \boldsymbol{x})$. $\boldsymbol{R}$ represents the coordinates of the nuclei and $\boldsymbol{x}$ represents the coordinates of the electrons. H' is the molecular Hamiltonian which is given by

$$H' = T_N + T_e + V_{ee} + V_{NN} + V_{Ne} \tag{2.2}$$

and E' is the total energy of the diatom which includes the kinetic energy of the center of mass and all internal energies. The terms in the Hamiltonian are the nuclear kinetic energy, the electronic kinetic energy, the nuclear-nuclear Coulombic repulsion, the nuclear-electronic Coulombic attraction and the electronic-electronic Coulombic repulsion potential energies respectively. We shall be neglecting spin, relativistic effects and time dependence in our analysis.

2.1 MOLECULAR COORDINATE TRANSFORMATIONS FOR H_2

The hydrogen molecule, H_2, is composed of 2 protons and 2 electrons. If spin and relativistic effects are ignored, then the Hamiltonian describing the system is given by [63]

$$H' = \frac{1}{2M} \sum_{I=1}^{2} {\boldsymbol{P_I}}^2 + \frac{1}{2m} \sum_{i=1}^{2} {\boldsymbol{p_i}}^2 + \frac{1}{|\boldsymbol{x_1} - \boldsymbol{x_2}|} + \frac{1}{|\boldsymbol{R_1} - \boldsymbol{R_2}|} - \sum_{I,i=1,2} \frac{1}{|\boldsymbol{R_I} - \boldsymbol{x_i}|} \tag{2.3}$$

where $\boldsymbol{R_I}$ and $\boldsymbol{P_I}$ are the conjugate position and momentum operators for the protons respectively, and $\boldsymbol{x_i}$ and $\boldsymbol{p_i}$ are the corresponding operators for the electrons where $I, i = 1, 2$. The coordinates are defined with respect to a common origin in a space fixed frame. The masses of the protons are denoted by M and m respectively. We will be using Hartree atomic units throughout except where we want to include some of the qualifying symbols in our calculations. In this system of units [10]

$$e = m = \hbar = 4\pi\epsilon_0 = 1 \quad \text{and} \quad c = 1/\alpha = 137.036 \tag{2.4}$$

where α is the fine structure constant and $M/m = 1836.15$. We also will be suppressing the convention of labeling an operator with a "hat" so that $\hat{H} \rightarrow H$. We want to perform a coordinate transformation into a Jacobi coordinate system so that the Hamiltonian transforms to $H' \rightarrow H = T_C + T_N + H_{AD}$ where the three terms on the right hand side describe the motion of the center of mass, the relative motion of the nuclei and the adiabatic Hamiltonian respectively. In performing this transformation the dependence of the wavefuntion on the coordinates relative to the space fixed frame will transform as $\psi(\boldsymbol{R_I}, \boldsymbol{x_i}) \rightarrow \psi(\boldsymbol{R_C}, \boldsymbol{R}, \boldsymbol{r_i})$ where $\boldsymbol{R_C}$ is the coordinate of the center of mass of the diatom, $\boldsymbol{R}$ is the relative separation of the nuclei, and $\boldsymbol{r_i}$ is the location of an electron with respect to the center of mass of the nuclei.

We will first transform the kinetic portion of the Hamiltonian

$$H'_K = -\frac{1}{2M}\sum_I \nabla^2_{R_I} - \frac{1}{2m}\sum_i \nabla^2_{x_i} \tag{2.5}$$

where we have made the substitution $\boldsymbol{P} \rightarrow -i\boldsymbol{\nabla}_R$ and $\boldsymbol{p} \rightarrow -i\boldsymbol{\nabla}_x$ and the differentiations are performed in cartesian coordinates.

The equations we use for the transformation are [63]:

Center of mass of the molecule:

$$\boldsymbol{R_C} = \frac{M\sum_I \boldsymbol{R_I} + m\sum_i \boldsymbol{x_i}}{M_T} \quad \text{where} \quad M_T = 2(M+m). \tag{2.6}$$

Center of mass of the nuclei:

$$\boldsymbol{R_N} = \frac{M\sum_I \boldsymbol{R_I}}{2M}. \tag{2.7}$$

Relative separation:

$$\boldsymbol{R} = \boldsymbol{R_2} - \boldsymbol{R_1}. \tag{2.8}$$

Location of the ith electron with respect to center of mass of the nuclei:

$$\boldsymbol{r_i} = \boldsymbol{x_i} - \boldsymbol{R_N}. \tag{2.9}$$

In order to begin the transformation procedure, we apply the chain rule to the gradient operator for each of the coordinates to be transformed and then reapply this for the Laplacian. The wavefunctions are all considered to be smooth and continuous functions so that there is no difficulty in differentiation and that there is equality in mixed partials. An example of this where we have chosen any one of the cartesian coordinates is

$$\begin{aligned} -\frac{1}{2M}\boldsymbol{\nabla}_{R_1}\psi(\boldsymbol{R_I},\boldsymbol{r_i}) &= \\ &-\frac{1}{2M}\left[\frac{\partial R_C}{\partial R_1}\frac{\partial}{\partial R_C} + \frac{\partial R}{\partial R_1}\frac{\partial}{\partial R} + \frac{\partial r_1}{\partial R_1}\frac{\partial}{\partial r_1} + \frac{\partial r_2}{\partial R_1}\frac{\partial}{\partial r_2}\right]\psi(\boldsymbol{R_C},\boldsymbol{R},\boldsymbol{r_i}). \end{aligned} \tag{2.10}$$

This same procedure is to be repeated with regards to the coordinates R, r_1, and r_2 and then reapplied so that the Laplacian is derived. This leads to the following terms:

$$\begin{aligned} -\frac{1}{2M}\nabla^2_{R_1}\psi(\boldsymbol{R_I},\boldsymbol{r_i}) = &-\frac{1}{2M}\left[\left(\frac{M}{M_T}\right)^2\nabla^2_{R_C} + \nabla^2_R + \frac{1}{4}\nabla^2_{r_1} + \frac{1}{4}\nabla^2_{r_2}\right. \\ &- \frac{2M}{M_T}\boldsymbol{\nabla}_{R_C}\cdot\boldsymbol{\nabla}_R - \frac{M}{M_T}\boldsymbol{\nabla}_{R_C}\cdot\boldsymbol{\nabla}_{r_1} + \frac{M}{M_T}\boldsymbol{\nabla}_{R_C}\cdot\boldsymbol{\nabla}_{r_2} \\ &\left. + \boldsymbol{\nabla}_R\cdot\boldsymbol{\nabla}_{r_1} + \boldsymbol{\nabla}_R\cdot\boldsymbol{\nabla}_{r_2} + \frac{1}{2}\boldsymbol{\nabla}_{r_1}\cdot\boldsymbol{\nabla} r_2\right]\psi(\boldsymbol{R_C},\boldsymbol{R},\boldsymbol{r_i}), \end{aligned} \tag{2.11}$$

$$\begin{aligned} -\frac{1}{2M}\nabla^2_{R_2}\psi(\boldsymbol{R_I},\boldsymbol{r_i}) = &-\frac{1}{2M}\left[\left(\frac{M}{M_T}\right)^2\nabla^2_{R_C} + \nabla^2_R + \frac{1}{4}\nabla^2_{r_1} + \frac{1}{4}\nabla^2_{r_2}\right. \\ &+ \frac{2M}{M_T}\boldsymbol{\nabla}_{R_C}\cdot\boldsymbol{\nabla}_R - \frac{M}{M_T}\boldsymbol{\nabla}_{R_C}\cdot\boldsymbol{\nabla}_{r_1} + \frac{M}{M_T}\boldsymbol{\nabla}_{R_C}\cdot\boldsymbol{\nabla}_{r_2} \\ &\left. - \boldsymbol{\nabla}_R\cdot\boldsymbol{\nabla}_{r_1} - \boldsymbol{\nabla}_R\cdot\boldsymbol{\nabla}_{r_2} + \frac{1}{2}\boldsymbol{\nabla}_{r_1}\cdot\boldsymbol{\nabla} r_2\right]\psi(\boldsymbol{R_C},\boldsymbol{R},\boldsymbol{r_i}), \end{aligned} \tag{2.12}$$

$$-\frac{1}{2m}\nabla^2_{r_1}\psi(\boldsymbol{R_I},\boldsymbol{r_i}) = -\frac{1}{2m}\left[\left(\frac{m}{M_T}\right)^2\nabla^2_{R_C} + \nabla^2_{r_1} + \frac{2m}{M_T}\boldsymbol{\nabla}_{R_C}\cdot\boldsymbol{\nabla}_{r_1}\right]\psi(\boldsymbol{R_C},\boldsymbol{R},\boldsymbol{r_i}), \tag{2.13}$$

$$-\frac{1}{2m}\nabla^2_{r_2}\psi(\boldsymbol{R_I},\boldsymbol{r_i}) = -\frac{1}{2m}\left[\left(\frac{m}{M_T}\right)^2\nabla^2_{R_C} + \nabla^2_{r_2} + \frac{2m}{M_T}\boldsymbol{\nabla}_{R_C}\cdot\boldsymbol{\nabla}_{r_2}\right]\psi(\boldsymbol{R_C},\boldsymbol{R},\boldsymbol{r_i}). \tag{2.14}$$

Combining (2.11),(2.12),(2.13), and (2.14) rearranging and simplifying the kinetic portion of the Hamiltonian H'_K transforms as

$$H'_K \to H_K = -\left[\frac{1}{2M_T}\nabla^2_{R_C} + \frac{1}{2\mu}\nabla^2_R + \frac{1}{2m}\sum_i \nabla^2_{r_i} + \frac{1}{4M}\left(\sum_i \boldsymbol{\nabla}_{r_i}\right)^2\right] \tag{2.15}$$

where $\mu = M/2$ is the reduced mass of the nuclei. Using the coordinate transformations given in (2.8)-(2.9) the potential of H' transforms as

$$\begin{aligned}&\left[\frac{1}{|\boldsymbol{x_1} - \boldsymbol{x_2}|} + \frac{1}{|\boldsymbol{R_1} - \boldsymbol{R_2}|} - \sum_{I,i=1,2} \frac{1}{|\boldsymbol{R_I} - \boldsymbol{x_i}|}\right]\psi(\boldsymbol{R_I}, \boldsymbol{r_i}) \\ &\qquad = \left[\frac{1}{|\boldsymbol{r_1} - \boldsymbol{r_2}|} + \frac{1}{|\boldsymbol{R}|} - \sum_i \frac{1}{|\boldsymbol{r_i} \pm \boldsymbol{R}/2|}\right]\psi(\boldsymbol{R_C}, \boldsymbol{R}, \boldsymbol{r_i}). \end{aligned} \tag{2.16}$$

Combining (2.15) with (2.16) gives

$$H = T_C + T_N + H_{AD} \tag{2.17}$$

where

$$T_C = -\frac{1}{2M_T}\nabla^2_{R_C}, \tag{2.18}$$

$$T_N = -\frac{1}{2\mu}\nabla^2_R, \tag{2.19}$$

$$H_{AD} = -\frac{1}{2m}\sum_i \nabla^2_{r_i} - \frac{1}{4M}\left(\sum_i \boldsymbol{\nabla}_{r_i}\right)^2 + \frac{1}{|\boldsymbol{r_1} - \boldsymbol{r_2}|} + \frac{1}{|\boldsymbol{R}|} - \sum_i \frac{1}{|\boldsymbol{r_i} \pm \boldsymbol{R}/2|}. \tag{2.20}$$

T_C represents the kinetic energy of the diatom in free space and can be separated out of the total energy of the diatom. This then gives

$$T_N\,\psi(\boldsymbol{R}, \boldsymbol{r}) + H_{AD}\,\psi(\boldsymbol{R}, \boldsymbol{r}) = E\,\psi(\boldsymbol{R}, \boldsymbol{r}) \tag{2.21}$$

where E is the internal energy of the diatom. T_N represents the kinetic energy of the nuclei in regards to their relative separation and H_{AD} is the adiabatic Hamiltonian. (2.21) is the time-independent Schrödinger equation for the molecule. The second term of H_{AD} is the mass polarization and due to the factor $M >> m$, can usually be neglected. The remaining terms of H_{AD} can be written as in (2.2) so that

$$H_{AD} = T_e + V_{ee} + V_{NN} + V_{Ne} \tag{2.22}$$

which represent the 1st, 3rd, 4th, and 5th terms in (2.20) respectively.

2.2 THE BORN-OPPENHEIMER APPROXIMATION AND THE ADIABATIC HAMILTONIAN

It is impossible to obtain an analytic solution to the Schrödinger equation for a molecular system of coupled nuclear and electronic motion. The standard method to turn this into a tractable problem was done almost 80 years ago by Born and Oppenheimer [8].

The first step in this procedure is that the molecular wavefunction can be separated into nuclear and electronic components. This is described by [9]

$$\psi(\boldsymbol{R}, \boldsymbol{r}) = \sum_n \Phi_n(\boldsymbol{R}, \boldsymbol{r})\, F_n(\boldsymbol{R}). \tag{2.23}$$

The $\Phi_n(\boldsymbol{R}, \boldsymbol{r})$ are electronic wavefunctions which form a complete set of electronic eigenstates for the adiabatic Hamiltonian for a given value of $\boldsymbol{R}$ and the $F_n(\boldsymbol{R})$ are nuclear "wavefunctions" which are the expansion coefficients describing the amplitude of nuclear motion [9, 10, 61]. In an adiabatic treatment, the electronic motion is considered "fast" and the nuclear motion "slow" [5]. The electronic wavefunction is a function of the coordinates of the electrons, $\boldsymbol{r}$ and parametrically dependent on the internuclear separation vector, $\boldsymbol{R}$. The internuclear separation vector describes the separation of the nuclei and the orientation of the internuclear axis. It is given by the coordinates $\boldsymbol{R} = (R, \theta, \phi)$, thus the molecular wavefunction is dependent on all of these coordinates [63].

The nuclear "wavefunction" is not a wavefunction in the typical quantum mechanical sense due to how the basis functions are defined [5]. If we consider only a single state Born-Oppenheimer state then this wavefunction can be written as [8]

$$\psi(\boldsymbol{R}, \boldsymbol{r}) = \Phi(\boldsymbol{R}, \boldsymbol{r}) F(\boldsymbol{R}). \tag{2.24}$$

Substitution of (2.24) into (2.21) gives

$$T_N\, \Phi(\boldsymbol{R}, \boldsymbol{r}) F(\boldsymbol{R}) + H_{AD}\, \Phi(\boldsymbol{R}, \boldsymbol{r}) F(\boldsymbol{R}) = E\, \Phi(\boldsymbol{R}, \boldsymbol{r}) F(\boldsymbol{R}). \tag{2.25}$$

Let's expand the kinetic term of the adiabatic Hamiltonian.

$$\nabla_r^2\,\Phi(\boldsymbol{R},\boldsymbol{r})F(\boldsymbol{R}) = -\frac{1}{2m}\Big[\Phi(\boldsymbol{R},\boldsymbol{r})\nabla_r^2 F(\boldsymbol{R}) + \big(\nabla_r^2\Phi(\boldsymbol{R},\boldsymbol{r})\big)F(\boldsymbol{R}) + 2\boldsymbol{\nabla}_r\Phi(\boldsymbol{R},\boldsymbol{r})\cdot\boldsymbol{\nabla}_r F(\boldsymbol{R})\Big]. \tag{2.26}$$

Because the nuclear wavefunction is not dependent on electronic coordinates, $\nabla_r^2 F(\boldsymbol{R})$ and $\boldsymbol{\nabla}_r F(\boldsymbol{R})$ vanish and we are left with

$$\nabla_r^2\Phi(\boldsymbol{R},\boldsymbol{r})F(\boldsymbol{R}) = \big(\nabla_r^2\Phi(\boldsymbol{R},\boldsymbol{r})\big)F(\boldsymbol{R}) \tag{2.27}$$

and (2.25) becomes

$$\begin{aligned}
&-\frac{1}{2\mu}\nabla_R^2\big(\Phi(\boldsymbol{R},\boldsymbol{r})F(\boldsymbol{R})\big) + \Big[-\frac{1}{2m}\big(\nabla_r^2\Phi(\boldsymbol{R},\boldsymbol{r})\big)\\
&+ V_{ee}\Phi(\boldsymbol{R},\boldsymbol{r}) + V_{NN}\Phi(\boldsymbol{R},\boldsymbol{r}) + V_{Ne}\Phi(\boldsymbol{R},\boldsymbol{r})\Big]F(\boldsymbol{R})\\
&= E\,\Phi(\boldsymbol{R},\boldsymbol{r})F(\boldsymbol{R})
\end{aligned} \tag{2.28}$$

where we explicitly show the kinetic energy operator for the nuclei. The term in brackets is the adiabatic Hamiltonian.

The second step in the Born-Oppenheimer approximation is to solve the molecular Schrödinger equation for a given value of $\boldsymbol{R}$. If we imagine the nuclear motion of the molecule "frozen" in space, then the value of $\boldsymbol{R}$ is constant which means that the kinetic energy operator acting on the molecular wavefunction is zero. By applying this effect (2.28) becomes

$$-\frac{1}{2m}\nabla_r^2\Phi(\boldsymbol{R},\boldsymbol{r}) + V_{ee}\Phi(\boldsymbol{R},\boldsymbol{r}) + V_{NN}\Phi(\boldsymbol{R},\boldsymbol{r}) + V_{Ne}\Phi(\boldsymbol{R},\boldsymbol{r}) = \epsilon(R)\,\Phi(\boldsymbol{R},\boldsymbol{r}) \tag{2.29}$$

which is a time-independent Schrödinger equation for the electrons in a given nuclear configuration. As such it is an eigenvalue equation where $\epsilon(R)$ is called the Born-Oppenheimer energy and represents the energy of the electrons in this configuration and the electronic eigenstates are the solutions to the equation. The nuclei are now moved an infinitesimal amount to a new separation distance and again the electrons adjust to this new configuration. The step of solving the electronic Schrödinger equation is repeated and a new eigenenergy is found. This process is repeated in theory an infinite amount of times and as such the energy of the electrons as a function of internuclear separation is found, $\epsilon(R)$. The collection of all such curves is called a potential energy surface. This is considered an adiabatic process as the eigenstates of the electrons do not change under a slow variation of the internuclear separation [5, 7, 22]. In the absence of external fields, the potential operators are only dependent on the internuclear separation distance, R, and not the angular configuration (θ, ϕ) of the nuclei which is why $\epsilon(R)$ contains the scalar R [10]. The nuclear wavefunction was cancelled on both sides because the potential energy operators return scalar values and do not operate explicitly on the nuclear wavefunction.

The eigenenergy of the adiabatic Hamiltonian can now be substituted into (2.28) to give

$$-\frac{1}{2\mu}\nabla_R^2\big(\Phi(\boldsymbol{R},\boldsymbol{r})F(\boldsymbol{R})\big) + \epsilon(R)\,\Phi(\boldsymbol{R},\boldsymbol{r})F(\boldsymbol{R}) = E\,\Phi(\boldsymbol{R},\boldsymbol{r})F(\boldsymbol{R}). \tag{2.30}$$

In order to solve (2.30) for the nuclear wavefunction, the dependence on the electronic coordinates $\boldsymbol{r}$ needs to be eliminated. This can be accomplished by left multiplying (2.30) by the complex conjugate of the electronic wavefunction, $\Phi^*(\boldsymbol{R},\boldsymbol{r})$ and integrating over the electronic coordinates. Then (2.30) becomes

$$\begin{aligned} &-\frac{1}{2\mu}\int d^3r\,\Phi^*(\boldsymbol{R},\boldsymbol{r})\nabla_R^2\big(\Phi(\boldsymbol{R},\boldsymbol{r})F(\boldsymbol{R})\big) \\ &+\epsilon(R)\int d^3r\,\Phi^*(\boldsymbol{R},\boldsymbol{r})\Phi(\boldsymbol{R},\boldsymbol{r})F(\boldsymbol{R}) = E\int d^3r\,\Phi^*(\boldsymbol{R},\boldsymbol{r})\Phi(\boldsymbol{R},\boldsymbol{r})F(\boldsymbol{R}). \end{aligned} \tag{2.31}$$

Since the electronic wavefunctions form a complete set of electronic eigenstates for the adiabatic Hamiltonian, we can take them to be orthonormal so that [63]

$$\int d^3r\,\Phi^*(\boldsymbol{R},\boldsymbol{r})\Phi(\boldsymbol{R},\boldsymbol{r}) = 1 \tag{2.32}$$

and (2.31) simplifies to

$$-\frac{1}{2\mu}\int d^3r\,\Phi^*(\boldsymbol{R},\boldsymbol{r})\nabla_R^2\big(\Phi(\boldsymbol{R},\boldsymbol{r})F(\boldsymbol{R})\big) + \epsilon(R)\,F(\boldsymbol{R}) = E\,F(\boldsymbol{R}). \tag{2.33}$$

We will explicitly insert the nuclear kinetic energy operator into (2.33).

The Laplacian in spherical coordinates is given by [1]

$$\nabla_R^2 = \frac{1}{R^2}\frac{\partial}{\partial R}\Big(R^2\frac{\partial}{\partial R}\Big) + \frac{1}{R^2\sin^2\theta}\bigg[\sin\theta\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial}{\partial\theta}\Big) + \frac{\partial^2}{\partial\phi^2}\bigg]. \tag{2.36}$$

The first term in the Laplacian is the radial component and the second term is the angular component.

The angular component is the square of the nuclear angular momentum operator

$$\boldsymbol{N}^2 = -\frac{1}{\sin^2\theta}\bigg[\sin\theta\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial}{\partial\theta}\Big) + \frac{\partial^2}{\partial\phi^2}\bigg]. \tag{2.37}$$

Substituting (2.37) into (2.36) and then this into (2.33) gives

$$\frac{1}{2\mu R^2}\int d^3r\,\Phi^*(\boldsymbol{R},\boldsymbol{r})\bigg[-\frac{\partial}{\partial R}\Big(R^2\frac{\partial}{\partial R}\Big) + \boldsymbol{N}^2\bigg]\big(\Phi(\boldsymbol{R},\boldsymbol{r})F(\boldsymbol{R})\big) + \epsilon(R)\,F(\boldsymbol{R}) = E\,F(\boldsymbol{R}). \tag{2.38}$$

The term in brackets, which is the nuclear kinetic energy operator, is still acting on the electronic wavefunction.

The third step in the Born-Oppenheimer approximation uses the "fast" and "slow" adiabatic motion of the electrons and nuclei [5, 8–10]. Due to the mass of the nuclei being on the order of 10^3 times the mass of the electrons, the electrons are considered to adjust their postition instantaneously with regards to the radial nuclear motion. As such (2.38) becomes

$$\frac{1}{2\mu R^2}\bigg[-\frac{\partial}{\partial R}\Big(R^2\frac{\partial}{\partial R}\Big) + \int d^3r\,\Phi^*(\boldsymbol{R},\boldsymbol{r})\boldsymbol{N}^2\Phi(\boldsymbol{R},\boldsymbol{r})\bigg]F(\boldsymbol{R}) + \epsilon(R)\,F(\boldsymbol{R}) = E\,F(\boldsymbol{R}). \tag{2.39}$$

The term

$$\int d^3r\,\Phi^*(\boldsymbol{R},\boldsymbol{r})\boldsymbol{N}^2\Phi(\boldsymbol{R},\boldsymbol{r}) \tag{2.40}$$

is diagonal and doesn't couple different Born-Oppenheimer electronic states in the single channel Born-Oppenheimer approximation so is equivalent to $\boldsymbol{N}^2$. Eq. (2.39) is kept in this form

---

[1] There are three equivalent forms for the radial differential operator and two equivalent forms for the angular differential operator of the Laplacian in spherical coordinates. These are given by

$$\frac{1}{R^2}\frac{\partial}{\partial R}\Big(R^2\frac{\partial}{\partial R}\Big) \equiv \frac{1}{R}\frac{\partial^2}{\partial R^2}R \equiv \frac{\partial^2}{\partial R^2} + \frac{2}{R}\frac{\partial}{\partial R}, \tag{2.34}$$

and

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial}{\partial\theta}\Big) \equiv \frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta}. \tag{2.35}$$

because in the next section we will relate the nuclear angular momentum to a combination of total molecular angular momentum and electronic angular momentum, the projections of which act on the electronic wavefunctions and modify the Born-Oppenheimer energy, $\epsilon(R)$.

The equations (2.33) - (2.40) can be described in a slightly more transparent form. Expanding (2.33) gives

$$-\frac{1}{2\mu}\int d^3r\,\Phi^*(\boldsymbol{R},\boldsymbol{r})\Big[\Phi(\boldsymbol{R},\boldsymbol{r})\nabla_R^2 F(\boldsymbol{R}) + \big(\nabla_R^2\Phi(\boldsymbol{R},\boldsymbol{r})\big)F(\boldsymbol{R}) + 2\boldsymbol{\nabla}_R\Phi(\boldsymbol{R},\boldsymbol{r})\cdot\boldsymbol{\nabla}_R F(\boldsymbol{R})\Big] + \epsilon(R)\,F(\boldsymbol{R}) = E\,F(\boldsymbol{R}). \quad (2.41)$$

The third step of the Born-Oppenheimer approximation implies that the terms

$$-\frac{1}{2\mu}\int d^3r\,\Phi^*(\boldsymbol{R},\boldsymbol{r})\big(\nabla_R^2\Phi(\boldsymbol{R},\boldsymbol{r})\big)F(\boldsymbol{R}) \quad \text{and} \quad -\frac{1}{\mu}\int d^3r\,\Phi^*(\boldsymbol{R},\boldsymbol{r})\boldsymbol{\nabla}_R\Phi(\boldsymbol{R},\boldsymbol{r})\cdot\boldsymbol{\nabla}_R F(\boldsymbol{R}) \quad (2.42)$$

are considered to be negligible and ignored. These terms couple electronic and nuclear motion and are called the non-adiabatic coupling terms [11, 32]. Applying these approximations reduces (2.41) to

$$-\frac{1}{2\mu}\nabla_R^2 F(\boldsymbol{R}) + \epsilon(R)F(\boldsymbol{R}) = E\,F(\boldsymbol{R}). \quad (2.43)$$

This is now the Schrödinger equation for the nuclear wavefunction where $\epsilon(R)$ is now an effective scalar potential due to the internuclear separation of the nuclei and the electron charge distribution for this given configuraton. It gives rise to a force on the nuclei in the direction along the axis of internuclear separation called the Hellman-Feynman force and is given by [24]

$$\boldsymbol{F}_R = -\boldsymbol{\nabla}_R\,\epsilon(R). \quad (2.44)$$

Chapter 3

BORN OPPENHEIMER APPROXIMATION AND NON-ADIABATIC COUPLING

For a more complete treatment of the Born-Oppenheimer approximation, the non-adiabatic coupling of nuclear and electronic motion needs to be considered. These terms were neglected in the third step of the Born-Oppenheimer approximation in (2.39)-(2.42). The inclusion of these terms will lead to a modification of the Born-Oppenheimer energy, $\epsilon(R)$ in (2.43) [16, 17, 32, 50]. From (2.39) we recall that the nuclear angular momentum operator acts on the electronic wavefunctions. Also the electronic wavefunction is given by $\Phi(\boldsymbol{R}, \boldsymbol{r})$ where $\boldsymbol{R} = (R, \theta, \phi)$ and the energy is only dependent on the internuclear separation R. This means that the electronic wavefunction is described by the orientation in space of the diatom. In the molecular motion we are examining, we are assuming Hund's case (d) [10, 33]. In this scheme the electronic angular momentum, $\boldsymbol{L}$, is not coupled to the internuclear axis, $\boldsymbol{R}$, but is instead coupled to the nuclear angular momentum, $\boldsymbol{N}$, to give the total angular momentum, $\boldsymbol{J}$, so that

$$\boldsymbol{J} = \boldsymbol{N} + \boldsymbol{L}$$

or

$$\boldsymbol{N} = \boldsymbol{J} - \boldsymbol{L} \tag{3.1}$$

where $\boldsymbol{N}$ is perpendicular to the internuclear axis from

$$\boldsymbol{N} = \boldsymbol{R} \times \boldsymbol{P} \quad \text{which leads to} \quad \boldsymbol{N} \cdot \boldsymbol{R} = 0. \tag{3.2}$$

We now briefly discuss some aspects of the electronic wavefunctions in an arbitrary orientation.

3.1 MOLECULAR FRAME

In an atomic system the electronic angular momentum, $\boldsymbol{L^2}$, commutes with the Hamiltonian. The projection of the angular momentum along any one axis, usually chosen to be the z-axis, also commutes with the Hamiltonian and the orbital angular momentum so that eigenfunctions describing the atom can be constructed and the energy levels of an atom found.

In a diatom the two-center Coulomb interaction breaks spherical symmetry and L^2 no longer commutes with the electronic Hamiltonian, though the component of L along the internuclear axis does. We can exploit the axial symmetry of the diatom to define a new coordinate frame. In this frame, the internuclear axis can be chosen to be z' and the x' and y' axes perpendicular to this. We now briefly discuss rotations.

In order to describe the rotation of a 3-D Cartesian coordinate system or the rotation of a 3 dimensional body, Euler's theorem needs to be used. This rotation operator can then then describe any possible orientation of this object or coordinate system.

Euler's Theorem: Every rotation $R \in SO(3)$ can be written as a product of three rotations [35]

$$R(\phi, \theta, \chi) = R_z(\phi) R_y(\theta) R_z(\chi) \tag{3.3}$$

where R_y, and R_z are rotation operators around the original space fixed axes give by $R_i(\alpha) = e^{i\alpha L_i}$. SO(3) represents the group of all 3 x 3 orthogonal matrices with real elements having a determinant of 1. The angles ϕ, θ, χ are known as the Euler angles and are defined for the ranges

$$0 \leq \phi, \chi \leq 2\pi, \ 0 \leq \theta \leq \pi.$$

The rotation operator is given by

$$R\left(\phi, \theta, \chi\right) = e^{i\phi J_z} e^{i\theta J_y} e^{i\chi J_z} \tag{3.4}$$

which is a unitary transformation [35]. There are many such ways of defining the rotation operator in terms of Euler angles. In terms of the Euler angles, the nuclear angular momentum operator is given by

$$\boldsymbol{N}^2 = -\frac{1}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial}{\partial\theta}\Big) + \Big(\frac{\partial^2}{\partial\phi^2} + \frac{\partial^2}{\partial\chi^2}\Big) - 2\cos\theta\frac{\partial^2}{\partial\phi\chi^2}\right]. \tag{3.5}$$

If instead of rotating a 3-D frame, we want to examine the rotation of a single axis, all three of the Euler angles are no longer required. This rotation can be parametrized in terms of the first two Euler angles (θ, ϕ) by taking the internuclear axis of the diatomic molecule that has it's center of mass at the origin to be aligned along the z-axis of a space fixed frame, then rotate this about the y-axis by the angle θ followed by a rotation about the z-axis by the angle ϕ. Traditionally rotations from a lab frame into a molecular frame were done by calculating how the coordinates transformed from one coordinate system to the other by using the chain rule on the angular momentum operators in the Laplacian. Details of this method can be found in various books on molecular mechanics, namely the references [10–12].

We will be using a method in our discussion that uses the rotation operator, which is a unitary transformation and it's effect on the electronic wavefunctions [5, 14, 35]. The rotation operator in this case is given by the unitary transformation $U = e^{i\phi L_z} e^{i\theta L_y} e^{-i\phi L_z}$. The first rotation $e^{-i\phi L_z}$ doesn't act on the diatom aligned along $(0, \phi)$ but is included for computational purposes. What this implies is that the rotation about the terms involving the derivatives of χ are zero in the lab frame and (3.5) reduces to (2.37).

Due to this axial symmetry, a projection of the angular momentum along the internuclear axis, $L_{z'}$ commutes with the adiabatic Hamiltonian, so that $[H_{AD}, L_{z'}] = 0$. It can be shown that in the molecular frame that [11]

$$L_{z'} = -i\frac{\partial}{\partial\chi} \quad \text{and} \quad L_z = i\frac{\partial}{\partial\phi} \tag{3.6}$$

from which the change in sign gives rise to the anomalous commutation relations [13, 20, 31, 50]. The azimuthal portion of the electronic wavefunction is of the form [10]

$$\Phi(\boldsymbol{R}, \boldsymbol{r}) \propto e^{-i\Lambda\phi} \tag{3.7}$$

and when (3.6) acts on (3.7) gives the eigenvalues ,

$$\begin{aligned} L_{z'}\,\Phi(\boldsymbol{R}, \boldsymbol{r}) &= M_L\,\Phi(\boldsymbol{R}, \boldsymbol{r}), \quad M_L = 0, \pm 1, \pm 2, \ldots \\ &= \pm\Lambda\,\Phi(\boldsymbol{R}, \boldsymbol{r}), \quad \Lambda = 0, 1, 2, \ldots \end{aligned} \tag{3.8}$$

and $\Lambda = |M_L|$.

When the internuclear axis is along the z-axis, the adiabatic Hamiltonian in this specific configuration is called the Born-Oppenheimer Hamiltonian and the electronic wavefunctions are the Born-Oppenheimer wavefunctions, whereas they are called the adiabatic Hamiltonian and wavefunctions respectively in any general orientation [61, 63, 64].

The homonuclear diatom has a horizontal mirror plane passing through the center of mass of the molecule An inversion of spatial coordinates across this mirror plane is parity inversion. The parity operator acting on an eigenstate has the effect of multiplying the eigenstate by ±1. The molecular term symbol is then also denoted by the label, g or u respectively. This number reflects whether the electronic wavefunction changes sign upon reflection through the mirror plane [10]. If the angular momentum projection eigenvalue is $\Lambda \geq 1$, these states of identical energy are called Lambda doublets.

3.2 NON-ADIABATIC CORRECTIONS

We are now in a position to re-examine (2.38) by taking into account the non-adiabatic coupling of the electronic and nuclear motion.

The radial portion of (2.43) can be written as [11, 16, 17]

$$-\frac{1}{2\mu R^2}\int d^3r\,\Phi^*(\boldsymbol{R},\boldsymbol{r})\frac{\partial}{\partial R}\Big(R^2\frac{\partial}{\partial R}\Big)\Phi(\boldsymbol{R},\boldsymbol{r}) = \frac{1}{2\mu}\int d^3r\left(\frac{\partial\Phi(\boldsymbol{R},\boldsymbol{r})}{\partial R}\right)^2 \tag{3.9}$$

or

$$\frac{1}{2\mu}\int d^3r\left(\frac{\partial\Phi(\boldsymbol{R},\boldsymbol{r})}{\partial R}\right)^2 = \frac{B(R)}{2\mu} \tag{3.10}$$

where

$$B(R) \equiv \int d^3r\left(\frac{\partial\Phi(\boldsymbol{R},\boldsymbol{r})}{\partial R}\right)^2. \tag{3.11}$$

The angular portion of (2.38) will be discussed below.

From (3.1) and (3.2) it can be seen that

$$J_{z'} = L_{z'}. \tag{3.12}$$

This means that the projection of the total angular momentum along the internuclear axis is the same as the projection of the electronic angular momentum along the same axis. In the absence of external forces, the expectation values of the total angular momentum for the molecular wavefunction, $\psi(\boldsymbol{R},\boldsymbol{r})$, as well as the projection of angular momentum along the internuclear axis can be represented by

$$\langle\psi^*(\boldsymbol{R},\boldsymbol{r})\boldsymbol{J}^2\,\psi(\boldsymbol{R},\boldsymbol{r})\rangle = J(J+1) \tag{3.13}$$

and

$$\langle \psi^*(\boldsymbol{R},\boldsymbol{r}) J_z\, \psi(\boldsymbol{R},\boldsymbol{r})\rangle = M \tag{3.14}$$

respectively as given in Eq. (1.3.6) of [33] where $-J \leq M_J \leq J$. Applying (3.8) to the molecular wavefunction $\psi(\boldsymbol{R},\boldsymbol{r})$ gives [10]

$$\begin{aligned} L_{z'}\, \psi(\boldsymbol{R},\boldsymbol{r}) &= F(\boldsymbol{R})\, L_{z'}\, \Phi(\boldsymbol{R},\boldsymbol{r}) \\ &= \pm\Lambda\psi(\boldsymbol{R},\boldsymbol{r}). \end{aligned} \tag{3.15}$$

From (3.12) and (3.15), $\psi(\boldsymbol{R},\boldsymbol{r})$ is also an eigenfunction of $J_{z'}$ so that

$$J_{z'}\, \psi(\boldsymbol{R},\boldsymbol{r}) = \pm\Lambda\, \psi(\boldsymbol{R},\boldsymbol{r}) \tag{3.16}$$

where $J = |\Lambda|, |\Lambda|+1, |\Lambda|+2, \ldots$.

Returning to the angular momentum component of the molecule (2.39) we can substitute into this the square of (3.1) to give

$$\int d^3r\, \Phi^*(\boldsymbol{R},\boldsymbol{r})\boldsymbol{N}^2\Phi(\boldsymbol{R},\boldsymbol{r})F(\boldsymbol{R}) = \int d^3r\, \Phi^*(\boldsymbol{R},\boldsymbol{r})\big(\boldsymbol{J}^2 + \boldsymbol{L}^2 - 2\,\boldsymbol{J}\cdot\boldsymbol{L}\big)\Phi(\boldsymbol{R},\boldsymbol{r})F(\boldsymbol{R}). \tag{3.17}$$

The term in brackets on the right side of (3.17) can be rearranged by using (3.12) to give

$$\boldsymbol{J}^2 + \boldsymbol{L}^2 - 2\,\boldsymbol{J}\cdot\boldsymbol{L} = \boldsymbol{J}^2 - L_{z'}^2 + L_{x'}^2 + L_{y'}^2 - 2\,J_{x'}L_{x'} - 2J_{y'}L_{y'}. \tag{3.18}$$

Using (3.13)-(3.16) and that the last two terms on the right of (3.18) are off diagonal terms which disappear since they are being integrated over a single state

$$\begin{aligned} \int d^3r\, \Phi^*(\boldsymbol{R},\boldsymbol{r})\boldsymbol{N}^2\Phi(\boldsymbol{R},\boldsymbol{r})F(\boldsymbol{R}) =& \Big[J(J+1) - \Lambda^2\Big]F(\boldsymbol{R}) \\ &+ \int d^3r\, \Phi^*(\boldsymbol{R},\boldsymbol{r})\big(L_{x'}^2 + L_{y'}^2\big)\Phi(\boldsymbol{R},\boldsymbol{r})F(\boldsymbol{R}). \end{aligned} \tag{3.19}$$

We label the term [61]

$$\Omega^2(R) = \int d^3r\, \Phi^*(\boldsymbol{R},\boldsymbol{r})\big(L_{x'}^2 + L_{y'}^2\big)\Phi(\boldsymbol{R},\boldsymbol{r}) \tag{3.20}$$

so that (3.19) becomes

$$\int d^3r\,\Phi^*(\boldsymbol{R},\boldsymbol{r})\boldsymbol{N}^2\Phi(\boldsymbol{R},\boldsymbol{r})F(\boldsymbol{R}) = \Big[J(J+1) - \Lambda^2 + \Omega^2(R)\Big]F(\boldsymbol{R}). \tag{3.21}$$

The first term on the right hand side is the centrifugal barrier contribution to the potential due to molecular rotation, the second term is a modification to the centrifugal potential, and third term which is a function of R is a modification of the Λ term.

The molecular Schrödinger equation can finally be expressed as an eigenvalue equation describing nuclear motion by substituting (3.21) into (2.39).

$$\left[-\frac{1}{2\mu R^2}\frac{\partial}{\partial R}\Big(R^2\frac{\partial}{\partial R}\Big) + \frac{J(J+1) - \Lambda^2 + \Omega^2(R)}{2\mu R^2}\right]F(\boldsymbol{R}) + \tilde{\epsilon}(R)\,F(\boldsymbol{R}) = E\,F(\boldsymbol{R}) \tag{3.22}$$

where

$$\tilde{\epsilon}(R) = \epsilon(R) + \frac{B(R)}{2\mu} \tag{3.23}$$

is the modified Born-Oppenheimer energy, the constituents of which are all for a given internuclear separation.

From (3.22) it can be seen that the Hamiltonian describing nuclear motion is

$$H_N = \frac{1}{2\mu R^2}\Big[-\frac{\partial}{\partial R}\Big(R^2\frac{\partial}{\partial R}\Big) + \boldsymbol{J}^2 - \Lambda^2 + \Omega^2(R)\Big] + \tilde{\epsilon}(R). \tag{3.24}$$

We have shown so far that the adiabatic Born-Oppenheimer approximation leads to an incomplete Hamiltonian for nuclear motion in a homo-nuclear diatom.The inclusion of non-adiabatic coupling in the calculation of the nuclear Hamiltonian accounts for terms which modify the Born-Oppenheimer energy and the centrifugal potential of the diatom.

Chapter 4

SOLUTION OF THE NUCLEAR WAVEFUNCTION

4.1 SEPARATION OF RADIAL AND ANGULAR WAVEFUNCTIONS

We are now in a position to solve the wave equation for nuclear motion given by

$$\left[\frac{1}{2\mu R^2}\left[-\frac{\partial}{\partial R}\Big(R^2\frac{\partial}{\partial R}\Big)+\boldsymbol{J}^2-\Lambda^2+\Omega^2(R)\right]+\tilde{\epsilon}(R)\right]F(\boldsymbol{R})=E\,F(\boldsymbol{R}). \tag{4.1}$$

The nuclear wavefunction can be separated into radial and angular components given by the ansatz

$$F(\boldsymbol{R})=\frac{F^{\Lambda}_{JM}(R)}{R}\,Y^{\Lambda}_{JM}(\theta\phi) \tag{4.2}$$

so that (4.1) becomes

$$\left[-\frac{1}{2\mu}\frac{d^2}{dR^2}+\frac{\boldsymbol{J}^2-\Lambda^2+\Omega^2(R)}{2\mu R^2}+\tilde{\epsilon}(R)\right]F^{\Lambda}_{JM}(R)\,Y^{\Lambda}_{JM}(\theta\phi)=E\,F^{\Lambda}_{JM}(R)\,Y^{\Lambda}_{JM}(\theta\phi). \tag{4.3}$$

The effect of the the $\frac{1}{R}$ term puts the radial differential equation into standard form. The separation of (4.3) into radial and angular components respectively becomes

$$\left[-\frac{1}{2\mu}\frac{d^2}{dR^2}+\tilde{\epsilon}(R)-E+\epsilon^{\Lambda}_{JM}(R)\right]F^{\Lambda}_{JM}(R)=0, \tag{4.4}$$

$$\left[\frac{1}{2\mu R^2}\left[\boldsymbol{J}^2-\Lambda^2+\Omega^2(R)\right]-\epsilon^{\Lambda}_{JM}(R)\right]Y^{\Lambda}_{JM}(\theta\phi)=0. \tag{4.5}$$

where the rotational eigenvalue, $\epsilon^{\Lambda}_{JM}(R)$, for a given J and Λ, is the separation constant. The radial portion of the equation has a potential curve, $\tilde{\epsilon}(R)$ that determines nuclear vibration. This can be shown to be described by an anharmonic oscillator, the Morse potential, in the presence of a centrifugal barrier with solutions given by the associated Laguerre polynomials [33, 38, 40]. The Morse potential has a minimum at the equilibrium internuclear separation, R_e. The rotational energy of (4.5) needs to be determined in order to solve (4.4). The rotational solutions will be shown to be the Wigner functions [21, 33, 49].

4.2 ANGULAR MOTION

4.2.1 SYMMETRIC TOP

The angular component of diatomic motion can be shown to be the wave equation of the symmetric top which will allow us to find the solutions to (4.5). The following discussion shows how the quantum mechanical symmetric top can be derived from the classical symmetric top. The kinetic energy of a classical symmetric top is given by [21]

$$T = \frac{1}{2}\left[\frac{p_\theta^2}{I_1} + \Big(\frac{\cos^2\theta}{I_1\sin^2\theta} + \frac{1}{I_3}\Big)p_\chi^2 + \frac{1}{I_1\sin^2\theta}p_\phi^2 - \frac{2\cos\theta}{I_1\sin^2\theta}p_\phi p_\chi\right] \tag{4.6}$$

where the p_i represent the generalized momenta with respect to the time derivatives of the Euler angles, i.e. $p_\phi = \frac{\partial T}{\partial \dot{\phi}}$ and the angles θ, ϕ, and χ represent rotations about the space fixed $x-$, $y-$, and $z-$axes respectively.

In order to quantize this equation, [13, 21, 34, 43] and obtain the Schrödinger equation for the symmetric top, the quantum mechanical transformation of momentum must be made $p_\phi \rightarrow -i\frac{\partial}{\partial\phi}$. There is a problem with making this direct substitution into the above equation as the generalized coordinates are defined in Cartesian coordinates and will lead to an incorrect form of the Schrödinger equation . Podolsky showed that the correct transformation is given by the "Podolsky trick". The Hamiltonian transforms as [12, 41]

$$H = -\frac{\hbar^2}{2}|g|^{-1/2}\frac{\partial}{\partial q^i}|g|^{1/2}g^{ij}\frac{\partial}{\partial q^j}$$

where $|g| = I_1 I_2 I_3 \sin^2\theta$ and g^{ij} is a metric tensor of the moments of inertia expressed in terms of Euler angles.

This then leads to the quantum mechanical transformation of the momentum in terms of Euler angles as $p_\phi^2 = -\frac{\partial^2}{\partial\phi^2}$, $p_\chi^2 = -\frac{\partial^2}{\partial\chi^2}$, and $p_\theta^2 = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)$. Suppressing $\hbar$ we now have the Schrödinger equation for a symmetric top

$$-\frac{1}{2I_1}\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \left(\frac{I_1}{I_3} + \frac{\cos^2\theta}{\sin^2\theta}\right)\frac{\partial^2}{\partial\chi^2} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} - \frac{2\cos\theta}{\sin^2\theta}\frac{\partial^2}{\partial\phi\chi^2}\right]\psi(\phi\theta\chi) = T\,\psi(\phi\theta\chi) \tag{4.7}$$

where T is the rotational kinetic energy of the top and $\psi(\phi\theta\chi)$ is the wavefunction of the top in the representation of the Euler angles.

The wavefunction can be separated into components dependent on the Euler angles as

$$\psi(\phi\theta\chi) = d^J_{M,\Lambda}(\theta)e^{i(M\phi+\Lambda\chi)}. \tag{4.8}$$

This substitution gives after applying the differential operators to the wavefunction

$$-\frac{1}{2I_1}\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \Big(\frac{I_1}{I_3} + \frac{\cos^2\theta}{\sin^2\theta}\Big)(-\Lambda^2) + \frac{1}{\sin^2\theta}\Big(-M^2 + 2M\Lambda\cos\theta\Big)\right] d^J_{M,\Lambda}(\theta)\, e^{i(M\phi+\Lambda\chi)} = T\, d^J_{M,\Lambda}(\theta)\, e^{i(M\phi+\Lambda\chi)}. \tag{4.9}$$

The exponential functions cancel and we have after rearranging

$$-\frac{1}{2I_1}\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} - \frac{1}{\sin^2\theta}\left(M^2 - 2M\Lambda\cos\theta + \Lambda^2\cos^2\theta\right) - \frac{I_1}{I_3}\Lambda^2\right] d^J_{M,\Lambda}(\theta) = T\, d^J_{M,\Lambda}(\theta). \tag{4.10}$$

Using $\Lambda^2\cos^2\theta = \Lambda^2 - \Lambda^2\sin^2\theta$

$$-\frac{1}{2I_1}\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} - \frac{1}{\sin^2\theta}\left(M^2 - 2M\Lambda\cos\theta + \Lambda^2\right) + \Lambda^2 - \frac{I_1}{I_3}\Lambda^2\right] d^J_{M,\Lambda}(\theta) = T\, d^J_{M,\Lambda}(\theta) \tag{4.11}$$

or after rearranging

$$-\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} - \frac{1}{\sin^2\theta}\Big(M^2 - 2M\Lambda\cos\theta + \Lambda^2\Big)\right] d^J_{M,\Lambda}(\theta) = \left[2TI_1 + \Lambda^2 - \frac{I_1}{I_3}\Lambda^2\right] d^J_{M,\Lambda}(\theta). \tag{4.12}$$

4.2.2 MOLECULAR ANGULAR MOMENTUM

The angular function given by

$$Y^\Lambda_{JM}(\theta\phi) = d^J_{M,\Lambda}(\theta)e^{iM\phi} \tag{4.13}$$

is also an eigenfunction for the molecular angular momentum operator, $\boldsymbol{J}^2$, for a given value of Λ where [10, 33] [1]

$$\boldsymbol{J}^2 = -\frac{1}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial}{\partial\theta}\Big) + \Big(\frac{\partial}{\partial\phi} - i\Lambda\cos\theta\Big)^2\right]. \tag{4.14}$$

---

[1] (4.13) and (4.14) are the same as (4.8) and (3.5) respectively after applying the differential operator $\frac{\partial}{\partial\chi}$.

Applying (4.14) to (4.13) gives the total molecular angular momentum eigenvalue, $J(J+1)$ as

$$-\left[\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} - \frac{1}{\sin^2\theta}\Big(M^2 - 2M\Lambda\cos\theta + \Lambda^2\Big)\right] d^J_{M,\Lambda}(\theta) = J(J+1)\, d^J_{M,\Lambda}(\theta). \tag{4.15}$$

A comparison (4.12) of (4.15) shows an equality between the eigenvalues of the symmetric top and the molecular angular momentum gives

$$2T\, I_1 + \Lambda^2 - \frac{I_1}{I_3}\Lambda^2 = J(J+1) \tag{4.16}$$

which can be rearranged for the symmetric top energy, T

$$T = \frac{J(J+1) - \Lambda^2}{2I_1} + \frac{\Lambda^2}{2I_3}. \tag{4.17}$$

If we now choose the molecule to be at the equilibrium distance, R_e we can make the substitution [61]

$$B \equiv \frac{1}{2I_1} \quad \text{where} \quad \frac{1}{2I_1} = \frac{1}{2\mu R_e^2}. \tag{4.18}$$

We can now compare the energy of the symmetric top, T in (4.17) and the energy eigenvalues for the nuclear motion, $\epsilon^{\Lambda}_{JM}(R)$ which gives [33, 49, 61]

$$\epsilon^{\Lambda}_{JM}(R) = B\left[J(J+1) - \Lambda^2\Big(1 - \frac{1}{I_3}\Big)\right], \tag{4.19}$$

$$I_3 = \frac{\Lambda^2}{\Omega^2(R_e)}.$$

or

$$\epsilon^{\Lambda}_{JM}(R) = B\left[J(J+1) - \Lambda^2\Big(1 - \Omega^2(R_e)\Big)\right] \tag{4.20}$$

It can be seen from (4.19) that the effect of the Lambda doublets, Λ^2 is to decrease the rotational energy of the diatom. The effect of $\Omega^2(R_e)$, which from (3.20) represents the motion of the electrons *parallel* to the z'-axis, increases the the rotational energy of the diatom which thus reduces the effect of the Lambda term. We can then write (4.19) as

$$\epsilon^{\Lambda}_{JM}(R) = B\Big[J(J+1) - \tilde{\Lambda}^2\Big] \quad \text{where} \quad \tilde{\Lambda}^2 \leq \Lambda^2. \tag{4.21}$$

The solution to the nuclear rotational wave equation (4.5), the $Y^{\Lambda}_{JM}(\theta\phi) = d^{J}_{M,\Lambda}(\theta)e^{iM\phi}$ where the $d^{J}_{M,\Lambda}(\theta)$ are found to be the Wigner functions which can be written in terms of the hypergeometric functions. These solutions can be found in [10, 33] or in texts on mathematical physics [1].

4.3 RADIAL MOTION

The radial motion of the diatoms is determined by the Born-Oppenheimer potential, $\tilde{\epsilon}(R)$. There are many potential curves that can be fit to this potential which has the overall shape of an anharmonic oscillator. References to various potentials can be found in [33]. At low vibrational energies, the potential can often be approximated by a harmonic oscillator, but this becomes less realistic as the vibrational energy increases. The harmonic oscillator doesn't take into account the Coulombic repulsion approaching infinity as the nuclear separation approaches zero or the molecule dissociating into two atoms as the nuclear separation increases. A potential commonly used that gives an accurate representation of diatomic vibrational motion is the Morse potential [38]. The solution by Morse was done not taking rotational motion into account, so that $J = 0$. This solution was expanded on by Pekeris to include rotational motion for $J \geq 1$. We will give a solution to the vibrational energy levels by approximating the Morse potential as a harmonic oscillator and apply a time-independent non-degenerate pertubation to it. In Appendix A we elaborate on a detailed derivation of Morse's analysis. In Appendix B we outline the method of Pekeris and in Appendix C proceed with a perturbation treatment of the former.

4.3.1 APPROXIMATING THE MORSE POTENTIAL AS A HARMONIC OSCILLATOR

A solution can now be obtained for (4.4) now that the energy for the rotational eigenvalues, $\epsilon^{\Lambda}_{JM}(R)$, has been found in (4.21). In this case we have $J = 0$, and since $J \geq |\Lambda|$, then $\epsilon^{\Lambda}_{JM}(R) = 0$. The form of the Morse potential is given by [38]

$$\tilde{\epsilon}(R) = W_{eq} + D\left[1 - e^{-\beta(r-r_e)}\right]^2 \tag{4.22}$$

where W_{eq} is the energy of the potential at the equilibrium separation distance, $R = R_e$, D is dissociation energy of the diatom and β is a force constant similar to that in a harmonic oscillator [10]. We will take the equilibrium energy W_{eq} to be zero so that (4.4) becomes after the substitutions given above

$$\left[-\frac{1}{2\mu}\frac{d^2}{dR^2} + D\left[1 - e^{-\beta(R-R_e)}\right]^2 - E\right]F^{\Lambda}_{JM}(R) = 0. \tag{4.23}$$

A Taylor series expansion of the Morse potential keeping the first two non-vanishing terms gives

$$\tilde{\epsilon}(R) \approx \beta^2(R - R_e)^2 - \beta^3(R - R_e)^3. \tag{4.24}$$

The harmonic oscillator solution to (4.23) is given by using the first term in (4.24). The Hamiltonian for this case is given by

$$H = -\frac{1}{2\mu}\frac{d^2}{dR^2} + D\beta^2(R - R_e)^2. \tag{4.25}$$

The general case for a quantum mechanical harmonic oscillator is given by

$$H = -\frac{1}{2\mu}\frac{d^2}{dR^2} + \frac{1}{2}k(R - R_e)^2 \tag{4.26}$$

where the angular frequency is $\omega = \sqrt{\frac{k}{\mu}}$. Comparing (4.25) and (4.26) we see that $k = 2D\beta^2$ thus

$$\omega = \sqrt{\frac{2D\beta^2}{\mu}}. \tag{4.27}$$

The vibrational energy eigenvalues, E_ν, for the harmonic oscillator approximation for

$$\left[-\frac{1}{2\mu}\frac{d^2}{dR^2} + 2D\,\beta^2(R - R_e)^2 - E_\nu\right]F^{\Lambda}_{JM}(R) = 0, \quad \nu = 0, 1, 2\ldots \tag{4.28}$$

where ν are the vibrational level quantum numbers are given by [10]

$$E_\nu = \omega\Big(\nu + \frac{1}{2}\Big), \quad \nu = 0, 1, 2, \ldots \tag{4.29}$$

The vibrational wavefunctions, $F^{\Lambda}_{JM}(R)_{\nu}$, are given by [10]

$$F^{\Lambda}_{JM}(R)_{\nu} = \left(\frac{\alpha}{\sqrt{\pi}2^n n!}\right)^{1/2} e^{-\alpha^2 R^2/2} H_{\nu}(\alpha R) \tag{4.30}$$

where $\alpha = (2\mu D\beta^2)^{1/4}$ and $H_{\nu}(\alpha R)$ are the Hermite polynomials given by [1]

$$H_{\nu}(x) = (-1)^{\nu} e^{(x)^2} \frac{d^{\nu} e^{-x^2}}{d(x)^{\nu}}, \quad x = \alpha R. \tag{4.31}$$

4.3.2 APPLICATION OF A PERTURBATION TO THE HARMONIC OSCILLATOR APPROXIMATION

As discussed earlier the harmonic oscillator only gives good approximations to the vibrational eigenenergies for low quantum numbers. Born-Oppenheimer energies for bound diatoms exhibit anharmonicity for larger values of vibrational quantum numbers, and a more accurate treatment can be realized by applying a perturbation to the harmonic oscillator. The full steps can be found in Appendix A and we will present the results here. If we use the expansion given in (4.24) and treat the third order term as a perturbation, we have the energy eigenvalues given by [47]

$$E_n \approx E^{(0)} + \left\langle n \middle| \hat{H}^{(1)} \middle| n \right\rangle + \sum_{k \neq n} \frac{\left| \left\langle k \middle| \hat{H}^{(1)} \middle| n \right\rangle \right|^2}{E^{(0)}_n - E^{(0)}_k}. \tag{4.32}$$

After applying raising and lowering operators to the vibrational energy eigenstates, then (4.32) becomes

$$\begin{aligned} E_n \approx E^{(0)} + \gamma^2 \bigg(& \frac{\left|\sqrt{(n)(n-1)(n-2)}\right|^2}{E^{(0)}_{n+3} - E^{(0)}_n} + \frac{\left|3n\sqrt{n}\right|^2}{E^{(0)}_{n+1} - E^{(0)}_n} \\ & + \frac{\left|(3n+3)\sqrt{(n+1)}\right|^2}{E^{(0)}_{n-1} - E^{(0)}_n} + \frac{\left|\sqrt{(n+1)(n+2)(n+3)}\right|^2}{E^{(0)}_{n-3} - E^{(0)}_n} \bigg). \end{aligned} \tag{4.33}$$

Simplifying this becomes

$$E_n \approx \omega\left(\nu + \frac{1}{2}\right) - \frac{\omega^2}{4D}\left[\frac{15}{8}\left(\nu + \frac{1}{2}\right)^2 + \frac{7}{32}\right]. \tag{4.34}$$

4.3.3 MORSE POTENTIAL FOR $J = 0$

Morse obtained an analytical solution to (4.23) [38]. The steps to solving the eigenvalues are given in Appendix B. The eigenvalues to this equation are given by

$$E_\nu = \omega\Big(\nu + \frac{1}{2}\Big) - \frac{\omega^2}{4D}\Big(\nu + \frac{1}{2}\Big)^2. \tag{4.35}$$

The wavefunction solutions are given by the associated Laguerre polynomials [33, 38]which can be found in texts on mathematical physics [1].

A comparison of (4.29) and (4.34) shows that the application of a perturbation to the harmonic oscillator has added a term which creates an anharmonicity in the eigenenergies. Namely the spacing between energy levels decreases as the vibrational quantum number increases. This anharmonicity is inherent in the vibrational eigenvalues of the Morse potential and it can be seen in a comparison of (4.34) and (4.35), that the constant term in (4.34) becomes less significant at higher vibrational quantum numbers.

4.3.4 MORSE POTENTIAL FOR $J \neq 0$

Pekeris obtained a solution to the nucelar Schrödinger equation with non-zero angular momentum [40]. The results of this are in Appendix C. We state the eigenvalue solutions here

$$\frac{E_{\nu,J}}{c} = \omega\left(\nu+\frac{1}{2}\right) - \chi\omega\left(\nu+\frac{1}{2}\right)^2 + B\big[J(J+1)-\Lambda^2\big] + D\big[J^2(J+1)-\Lambda^2\big]^2 - \alpha(\nu+1/2)J(J+1) \tag{4.36}$$

The wavefunction solutions are given by the associated Laguerre polynomials [33, 40] which can be found in texts on mathematical physics [1].

Chapter 5

GAUGE THEORIES

5.1 INTRODUCTION TO GAUGE THEORIES

We will now review how the Maxwell field couples to charged particles in the non-relativistic Schrödinger equation . In modern terminology, the latter describes a gauge theory and here we give a brief review of important concepts in an Abelian gauge theory. We will then apply these concepts to our discussion of molecular structure.

Gauge theory was initially developed by Weyl in 1918 in an attempt to explain that the magnitude of physical measurements at specific space-time points are relative and not absolute. The relation of this change in scale was called gauge invariance. With the development of modern quantum mechanics in the mid 1920's, it was realized by Weyl, Fock, London and later expanded upon by Dirac [18, 52] that instead of a relation of scale between space-time points, this could reflect a change in the phase of the wavefunction. The vector potential $\boldsymbol{A}(\boldsymbol{R})$ was realized to be a gauge potential which connected the phases of different points. In Dirac's 1931 paper, he used this idea to define magnetic monopoles in order to quantize electric charge.

The Hamiltonian determining the behaviour of the wavefunction in the Schrödinger equation must also be invariant under specific gauge transformations, namely simultaneous gauge transformations of the matter and gauge fields [5]. These transformations will be discussed below.

5.2 GAUGE TRANSFORMATIONS

The electromagnetic gauge theory is called an Abelian gauge theory [5]. This means that the gauge functions are composed of 1×1 matrices, or scalars and the gauge potential is a vector. Electromagnetism is then called the U(1) gauge group [5, 27, 37].

The matter field, or wavefunction transforms under a unitary transformation. This transformation is a phase shift, or a rotation in the complex plane. This can be shown as

$$F(\boldsymbol{R}) \to F'(\boldsymbol{R}) = e^{i\,\lambda(\mathbf{R})}F(\boldsymbol{R}) \tag{5.1}$$

where $F(\boldsymbol{R})$ and $F'(\boldsymbol{R})$ both have the same normalization [18] and $\lambda(\boldsymbol{R})$ is the gauge function. The transformation needs to be unitary so that the norm of the wavefunction remains unchanged under this transformation [18, 44]. The gauge function is in general a function of space and time, but since we are considering a time independent Hamiltonian, we will label $\lambda(R)$ as a function of position only.

The gauge field, or vector potential transforms in general as

$$\boldsymbol{A} \to \boldsymbol{A'} = U\boldsymbol{A}U^{-1} + i\,U\boldsymbol{\nabla}U^{-1} \tag{5.2}$$

where the gauge transformations U and U^{-1} are respectively given by

$$U = e^{i\,\lambda(\mathbf{R})} \quad \text{and} \quad U^{-1} = e^{-i\,\lambda(\mathbf{R})}. \tag{5.3}$$

In the U(1) case which is Abelian, U and U^{-1} are scalars and so commute with $\boldsymbol{A}$ so that (5.2) becomes

$$\boldsymbol{A} \to \boldsymbol{A'} = \boldsymbol{A} + i\,U\boldsymbol{\nabla}U^{-1}. \tag{5.4}$$

Inserting (5.3) into (5.4) and (5.4) finally becomes

$$\boldsymbol{A} \to \boldsymbol{A'} = \boldsymbol{A} + \boldsymbol{\nabla}\lambda \tag{5.5}$$

which is the gauge transformation seen in electromagnetic textbooks [30]. Thus the gradient of the gauge function is the electromagnetic vector potential.

The gauge transformation for the potential is generally given by a four-vector since the scalar potential $V(R)$ is the temporal component of the electromagnetic field and the gauge function is generally a function of time. Since we are considering the time independent case, the scalar potential transforms as

$$\epsilon(R) \to \epsilon'(R) = \epsilon(R) \tag{5.6}$$

and so is unchanged.

The elements of the gauge transformations are then given by (5.1) and (5.5).

The gauge transformations are required because the electromagnetic potentials are not unique, however the choice of gauge should not effect the observable fields, $\boldsymbol{E(R)}$ and $\boldsymbol{B(R)}$. We can show how the magnetic field is invariant under a gauge transformation. Maxwell's equations give us that [46]

$$\boldsymbol{\nabla} \cdot \boldsymbol{B} = 0. \tag{5.7}$$

This is shown more clearly because the magnetic field arises from a vector potential

$$\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A}. \tag{5.8}$$

So that

$$\boldsymbol{\nabla} \cdot \boldsymbol{\nabla} \times \boldsymbol{A} = 0 \tag{5.9}$$

which is known from vector calculus identities. The curl of the gradient of a scalar function is zero.

$$\boldsymbol{\nabla} \times \boldsymbol{\nabla}\lambda(\mathbf{R}) = 0 \tag{5.10}$$

where $\lambda(\mathbf{R})$ is the gauge function. The magnetic field is invariant under this transformation as can be shown. Let

$$\boldsymbol{A} \to \boldsymbol{A'} = \mathbf{A} + \boldsymbol{\nabla}\lambda(\mathbf{R}). \tag{5.11}$$

Taking the curl gives

$$\boldsymbol{B'} = \boldsymbol{\nabla} \times \boldsymbol{A'} = \boldsymbol{\nabla} \times \boldsymbol{A} + \boldsymbol{\nabla} \times \boldsymbol{\nabla}\lambda(\mathbf{R}) = \mathbf{B}. \tag{5.12}$$

5.3 INVARIANCE OF THE SCHRÖDINGER EQUATION

The electromagnetic potentials define the fields, but gauge theory also determines the interaction between the electromagnetic field and an electric charge [46]. This interaction should be invariant under the gauge transformations so that the expectation values of position and momentum do not change. This is not the case for the canonical momentum. The canonical momentum, $\boldsymbol{p} = -i\boldsymbol{\nabla}$ in the standard Schrödinger equation $H = \frac{1}{2\mu}\boldsymbol{p}^2$ needs to be replaced by the operator in the minimally coupled Hamiltonian. This term is called the kinematical momentum defined as [44]

$$\boldsymbol{\Pi} \equiv \boldsymbol{p} - \boldsymbol{A}. \tag{5.13}$$

Inserting (5.13) into the Hamiltonian for the nuclear Schrödinger equation gives

$$H = \frac{1}{2\mu}\boldsymbol{\Pi}^2 + \epsilon(R). \tag{5.14}$$

Noting that $\boldsymbol{p} = -i\boldsymbol{\nabla}$, (5.13) can be written as

$$\boldsymbol{\Pi} = -i\boldsymbol{\nabla} - \boldsymbol{A}(\boldsymbol{R}) = -i(\boldsymbol{\nabla} - i\,\boldsymbol{A}(\boldsymbol{R})) \tag{5.15}$$

where the *gauge covariant derivative* is defined as [15]

$$\boldsymbol{D} \equiv \boldsymbol{\nabla} - i\,\boldsymbol{A}(\boldsymbol{R}). \tag{5.16}$$

Eq. (5.15) has the commutation relation [15]

$$[D_j, D_k] = -i\,(\partial_j\,A_k - \partial_k\,A_j) = -i\,\epsilon_{jkl}\,B_l. \tag{5.17}$$

There are also the commutation relations [1] [15]

$$[R_j, R_k] = 0 \quad \text{and} \quad [R_j, D_k] = i\,\delta_{jk}. \tag{5.18}$$

The gauge covariant derivative can now be used to write the Born-Oppenheimer equation (5.30), in a form invariant (covariant) way [64]. Inserting (5.16) into (5.30) gives

$$-\frac{1}{2\mu}\boldsymbol{D}\cdot\boldsymbol{D}\,F(\boldsymbol{R}) + \tilde{\epsilon}(R)\,F(\boldsymbol{R}) = E\,F(\boldsymbol{R}). \tag{5.19}$$

It can be shown that the form of (5.19) is invariant under the transformations (5.1) and (5.5) and that the gauge covariant derivatives (5.16) transform like the wavefunction *cf.* (5.1) under the same transformations [5]. In general the gauge potential is written as a four-vector given by $A^\mu = (\tilde{\epsilon}, \boldsymbol{A})$ where $\tilde{\epsilon}$ is the 0^{th} component. Then the commutator of the gauge covariant

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[1] In a cartesian coordinate system $A_j = A^j$

derivatives give

$$[D_\mu, D_\nu] = -i\,(\partial_\mu\, A_\nu - \partial_\nu\, A_\mu) = i\, F_{\mu,\nu} \tag{5.20}$$

where $F_{\mu,\nu}$ is the electromagnetic field strength tensor for the electromagnetic fields [26]

$$\boldsymbol{E} = -\boldsymbol{\nabla}\, A_0 - \partial_0\, \boldsymbol{A}, \quad \boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A}. \tag{5.21}$$

5.4 GAUGE THEORY OF NON-ADIABATIC COUPLING TERMS

We are now in want to examine the treatment of diatomic motion using gauge theory. The application of gauge theory to the motion of diatoms was first done by Moody, Shapere, and Wilczek [37]. This technique was expanded upon in [29, 61, 64]. In this section we want to show that (2.38) can be written in terms of gauge potentials.

We now return to (2.33) examine the non-adiabatic coupling terms using gauge theory. Expanding out the first term in (2.33) gives

$$\begin{aligned} -\frac{1}{2\mu}\Big[\nabla_R^2 F(\boldsymbol{R}) &+ \Big(\int d^3r\, \Phi^*(\boldsymbol{R},\boldsymbol{r})\nabla_R^2\Phi(\boldsymbol{R},\boldsymbol{r})\Big)\, F(\boldsymbol{R}) \\ &+ 2\Big(\int d^3r\, \Phi^*(\boldsymbol{R},\boldsymbol{r})\boldsymbol{\nabla}_R\Phi(\boldsymbol{R},\boldsymbol{r})\Big)\cdot \boldsymbol{\nabla}_R F(\boldsymbol{R})\Big] + \epsilon(R)\, F(\boldsymbol{R}) = E\, F(\boldsymbol{R}). \end{aligned} \tag{5.22}$$

We now make the following definitions [64]

$$\boldsymbol{A}(\boldsymbol{R}) \equiv i\int d^3r\, \Phi^*(\boldsymbol{R},\boldsymbol{r})\boldsymbol{\nabla}_R\Phi(\boldsymbol{R},\boldsymbol{r}) \tag{5.23}$$

and

$$B(\boldsymbol{R}) \equiv -\int d^3r\, \Phi^*(\boldsymbol{R},\boldsymbol{r})\nabla_R^2\Phi(\boldsymbol{R},\boldsymbol{r}). \tag{5.24}$$

Substituting these into (5.22) and rearranging gives

$$-\frac{1}{2\mu}\Big[\nabla_R^2 - 2i\boldsymbol{A}(\boldsymbol{R})\cdot\boldsymbol{\nabla}_R - B(\boldsymbol{R})\Big]F(\boldsymbol{R}) + \epsilon(R)\, F(\boldsymbol{R}) = E\, F(\boldsymbol{R}). \tag{5.25}$$

Using the identity [64]

$$B_{ij}(\boldsymbol{R}) = \sum_k \boldsymbol{A}_{ik}\cdot\boldsymbol{A}_{kj} + i\boldsymbol{\nabla}\cdot\boldsymbol{A}_{ij}$$

or

$$B_{ij}(\boldsymbol{R}) = \sum_{k\neq 1} \boldsymbol{A}_{ik}\cdot\boldsymbol{A}_{kj} + \boldsymbol{A}_{i1}\cdot\boldsymbol{A}_{1j} + i\boldsymbol{\nabla}\cdot\boldsymbol{A}_{ij}. \tag{5.26}$$

Using the single electronic state where $i = j = 1$ this becomes

$$B(\boldsymbol{R}) = \boldsymbol{A}\cdot\boldsymbol{A} + i\boldsymbol{\nabla}\cdot\boldsymbol{A} + \sum_{k\neq 1}\boldsymbol{A}_{1k}\cdot\boldsymbol{A}_{k1}. \tag{5.27}$$

Substituting (5.27) into (5.25) and rearranging gives

$$\begin{aligned} -\frac{1}{2\mu}\Big[\nabla_R^2 - i\boldsymbol{\nabla}_R\cdot\boldsymbol{A}(\boldsymbol{R}) - 2i\boldsymbol{A}(\boldsymbol{R})\cdot\boldsymbol{\nabla}_R - \boldsymbol{A}(\boldsymbol{R})\cdot\boldsymbol{A}(\boldsymbol{R})\Big]F(\boldsymbol{R}) + \epsilon(R)\,F(\boldsymbol{R}) \\ + \frac{1}{2\mu}\sum_{k\neq 1}\big(\boldsymbol{A}_{1k}\cdot\boldsymbol{A}_{k1}\big)\,F(\boldsymbol{R}) = E\,F(\boldsymbol{R}). \end{aligned} \tag{5.28}$$

Lets expand the following

$$\big[\boldsymbol{\nabla}_R - i\boldsymbol{A}(\boldsymbol{R})\big]^2 F(\boldsymbol{R}) = \big[\nabla_R^2 - i\boldsymbol{\nabla}_R\cdot\boldsymbol{A}(\boldsymbol{R}) - 2i\boldsymbol{A}\cdot\boldsymbol{\nabla}_R - \boldsymbol{A}(\boldsymbol{R})\cdot\boldsymbol{A}(\boldsymbol{R})\big]\,F(\boldsymbol{R}) \tag{5.29}$$

which is what we have in (5.28) such that (5.28) becomes

$$-\frac{1}{2\mu}\big[\boldsymbol{\nabla}_R - i\boldsymbol{A}(\boldsymbol{R})\big]^2 F(\boldsymbol{R}) + \tilde{\epsilon}(R)\,F(\boldsymbol{R}) = E\,F(\boldsymbol{R}) \tag{5.30}$$

where [37]

$$\tilde{\epsilon}(R) = \epsilon(R)\,F(\boldsymbol{R}) + \frac{1}{2\mu}\sum_{k\neq 1}\big(\boldsymbol{A}(\boldsymbol{R})_{1k}\cdot\boldsymbol{A}(\boldsymbol{R})_{k1}\big)\,F(\boldsymbol{R}). \tag{5.31}$$

So we see that by including the non-adiabatic coupling terms the Schrödinger equation has taken on a gauge potential that now acts on the nuclei and the electric potential is now modified by a scalar term from the vector potential. We will show in sections 8.1 and 8.2 that the traditional non-adiabatic coupling terms arise out of the gauge fields present in a rotating diatom.

Chapter 6

MAGNETIC MONOPOLES IN DIATOMS

6.1 ROTATION OF THE ELECTRONIC WAVEFUNCTIONS

In chapter 3.1, we described the orientation of a diatomic molecule and how its related to the Euler angles. In this chapter we will describe how the electronic wavefunctions transform under these rotations. We shall label the the electronic wavefunction by their eigenstates in this chapter. The eigenstates are labeled by the value of their electronic angular momentum projection on the internuclear axis of the diatom, Λ [61]. In $|\pm\Phi_\Lambda(0,\phi)\rangle$ the notation $(0,\phi)$ represents that until a rotation about θ occurs ϕ can take on all possible values. The symbol $\pm\Phi$ represents whether Λ is ± [61]. This can be shown as [3, 5, 61]

$$|\pm\Phi_\Lambda(\theta,\phi)\rangle = U_+ |\pm\Phi_\Lambda(0,\phi)\rangle = e^{i\phi L_z} e^{i\theta L_y} e^{-i\phi L_z} |\pm\Phi_\Lambda(0,\phi)\rangle \,, \tag{6.1}$$

and also

$$\langle\pm\Phi_\Lambda(\theta,\phi)| = \langle\pm\Phi_\Lambda(0,\phi)| \, U_+^{-1} = \langle\pm\Phi_\Lambda(0,\phi)| \, e^{i\phi L_z} e^{-i\theta L_y} e^{-i\phi L_z}. \tag{6.2}$$

This rotation describes all possible orientations of the molecule uniquely except at the angle $\theta = \pi$. A different transformation can be used to uniquely describe all orientations except those given for $\theta = 0$ [3, 5]. This is

$$|\pm\Phi_\Lambda(\theta,\phi)\rangle = U_- |\pm\Phi_\Lambda(0,\phi)\rangle = e^{i\phi L_z} e^{i\theta L_y} e^{i\phi L_z} |\pm\Phi_\Lambda(0,\phi)\rangle \tag{6.3}$$

with

$$\langle\pm\Phi_\Lambda(\theta,\phi)| = \langle\pm\Phi_\Lambda(0,\phi)| \, U_-^{-1} = \langle\pm\Phi_\Lambda(0,\phi)| \, e^{-i\phi L_z} e^{-i\theta L_y} e^{-i\phi L_z}. \tag{6.4}$$

The states described by $|\pm\Phi_\Lambda(0,\phi)\rangle$ are called the electronic Born-Oppenheimer eigenstates and the states given by $|\pm\Phi_\Lambda(\theta,\phi)\rangle$ are called the electronic adiabatic eigenstates [61]. We will denote the regions where (6.1) and (6.2) hold as R_+, and where (6.3) and (6.4) hold as R_-.

6.2 MAGNETIC MONOPOLE FIELD FROM A GAUGE POTENTIAL

We want to now see what form the gauge potential, $\boldsymbol{A}(\boldsymbol{R})$ that was defined in (5.23) and emerged in the molecular Hamiltonian, (5.30) and (5.31) takes by transforming it from a space fixed frame to a body fixed frame for an arbitrary orientation. After doing this we can see the effect this has on the adiabatic eigenstates with eigenvalues ±Λ [37, 61]. Thus we transform

$$\boldsymbol{A}(\boldsymbol{R}) = i\,\langle \pm\Phi_\Lambda(0,\phi)|\, U^{-1}\boldsymbol{\nabla}_R U\, |\pm\Phi_\Lambda(0,\phi)\rangle \rightarrow i\,\langle \pm\Phi_\Lambda(\theta,\phi)|\, \boldsymbol{\nabla}_R\, |\pm\Phi_\Lambda(\theta,\phi)\rangle\,. \tag{6.5}$$

Expanding out (6.5) we have

$$\begin{aligned}\boldsymbol{A}(\boldsymbol{R}) = i\,\langle \pm\Phi_\Lambda(\theta,\phi)|\, \hat{\mathbf{R}}\frac{\partial}{\partial R}\, |\pm\Phi_\Lambda(\theta,\phi)\rangle + i\,\langle \pm\Phi_\Lambda(\theta,\phi)|\, \frac{\hat{\boldsymbol{\theta}}}{R}\frac{\partial}{\partial\theta}\, |\pm\Phi_\Lambda(\theta,\phi)\rangle \\ + i\,\langle \pm\Phi_\Lambda(\theta,\phi)|\, \frac{\hat{\boldsymbol{\phi}}}{R\sin\theta}\frac{\partial}{\partial\phi}\, |\pm\Phi_\Lambda(\theta,\phi)\rangle\,.\end{aligned} \tag{6.6}$$

We can now see how each of the components of $\boldsymbol{A}(\boldsymbol{R})$ act under the unitary transformations. In the following calculations we will use the Baker-Campbell-Hausdorff relation.

$$e^{i\alpha L_j/\hbar}L_k e^{-i\alpha L_j/\hbar} = L_k + \frac{i\alpha}{\hbar}[L_j, L_k] + (\frac{i\alpha}{\hbar})^2[L_j,[L_j,L_k] + (\frac{i\alpha}{\hbar})^3[L_j,[L_j,[L_j,L_k]]] + \ldots. \tag{6.7}$$

Eq. (6.7) along with the angular momentum commutation relations [35]

$$[L_j, L_k] = i\,\epsilon_{jk}{}^{l}L_l \quad \text{and using the complex conjugate}$$

gives the identity

$$e^{\mp i\alpha L_j/\hbar}L_k e^{\pm i\alpha L_j/\hbar} = (\cos\alpha)L_k \pm \epsilon_{jk}{}^{l}(\sin\alpha)L_l. \tag{6.8}$$

For R_+:

$\hat{\mathbf{R}}$:

$$i\,\langle \pm\Phi_\Lambda(\theta,\phi)|\, \frac{\partial}{\partial R}\, |\pm\Phi_\Lambda(\theta,\phi)\rangle = i\,\langle \pm\Phi_\Lambda(0,\phi)|\, e^{i\phi L_z}e^{-i\theta L_y}e^{-i\phi L_z}\frac{\partial}{\partial R}e^{i\phi L_z}e^{i\theta L_y}e^{-i\phi L_z}\, |\pm\Phi_\Lambda(0,\phi)\rangle$$

$$i\,\langle \pm\Phi_\Lambda(\theta,\phi)|\, \frac{\partial}{\partial R}\, |\pm\Phi_\Lambda(\theta,\phi)\rangle = i\,\langle \pm\Phi_\Lambda(0,\phi)|\, \frac{\partial}{\partial R}\, |\pm\Phi_\Lambda(0,\phi)\rangle\,. \tag{6.9}$$

$\hat{\boldsymbol{\theta}}$:

$$\begin{aligned}
i \langle \pm\Phi_\Lambda(\theta,\phi)| \frac{\partial}{\partial\theta} |\pm\Phi_\Lambda(\theta,\phi)\rangle &= i \langle \pm\Phi_\Lambda(0,\phi)| e^{i\phi L_z} e^{-i\theta L_y} e^{-i\phi L_z} \frac{\partial}{\partial\theta} e^{i\phi L_z} e^{i\theta L_y} e^{-i\phi L_z} |\pm\Phi_\Lambda(0,\phi)\rangle \\
&= - \langle \pm\Phi_\Lambda(0,\phi)| e^{i\phi L_z} L_y e^{-i\phi L_z} |\pm\Phi_\Lambda(0,\phi)\rangle \\
i \langle \pm\Phi_\Lambda(\theta,\phi)| \frac{\partial}{\partial\theta} |\pm\Phi_\Lambda(\theta,\phi)\rangle &= - \langle \pm\Phi_\Lambda(0,\phi)| L_y \cos\phi + L_x \sin\phi |\pm\Phi_\Lambda(0,\phi)\rangle . \qquad (6.10)
\end{aligned}$$

$\hat{\boldsymbol{\phi}}$:

$$\begin{aligned}
i \langle \pm\Phi_\Lambda(\theta,\phi)| \frac{\partial}{\partial\phi} |\pm\Phi_\Lambda(\theta,\phi)\rangle &= i \langle \pm\Phi_\Lambda(0,\phi)| e^{i\phi L_z} e^{-i\theta L_y} e^{-i\phi L_z} \frac{\partial}{\partial\phi} e^{i\phi L_z} e^{i\theta L_y} e^{-i\phi L_z} |\pm\Phi_\Lambda(0,\phi)\rangle \\
&= - \langle \pm\Phi_\Lambda(0,\phi)| e^{i\phi L_z} e^{-i\theta L_y} L_z e^{i\theta L_y} e^{-i\phi L_z} - L_z |\pm\Phi_\Lambda(0,\phi)\rangle \\
&= - \langle \pm\Phi_\Lambda(0,\phi)| e^{i\phi L_z} (L_z \cos\theta + L_x \sin\theta) e^{-i\phi L_z} - L_z |\pm\Phi_\Lambda(0,\phi)\rangle \\
&= - \langle \pm\Phi_\Lambda(0,\phi)| L_z \cos\theta - L_z + L_x \sin\theta\cos\phi - L_y \sin\theta\sin\phi |\pm\Phi_\Lambda(0,\phi)\rangle \\
i \langle \pm\Phi_\Lambda(\theta,\phi)| \frac{\partial}{\partial\phi} |\pm\Phi_\Lambda(\theta,\phi)\rangle &= (1-\cos\theta) \langle \pm\Phi_\Lambda(0,\phi)| L_z |\pm\Phi_\Lambda(0,\phi)\rangle \\
&\quad + \langle \pm\Phi_\Lambda(0,\phi)| L_y \sin\theta\sin\phi - L_x \sin\theta\cos\phi |\pm\Phi_\Lambda(0,\phi)\rangle . \qquad (6.11)
\end{aligned}$$

Now combining (6.9), (6.10), and (6.11) into (6.6) we get

$$\begin{aligned}
\boldsymbol{A}(\boldsymbol{R})_+ = i\,\hat{\mathbf{R}} \langle \pm\Phi_\Lambda(0,\phi)| \frac{\partial}{\partial R} |\pm\Phi_\Lambda(0,\phi)\rangle - \frac{\hat{\boldsymbol{\theta}}}{R} \langle \pm\Phi_\Lambda(0,\phi)| L_y \cos\phi + L_x \sin\phi |\pm\Phi_\Lambda(0,\phi)\rangle \\
+ \frac{\hat{\boldsymbol{\phi}}(1-\cos\theta)}{R\sin\theta} \langle \pm\Phi_\Lambda(0,\phi)| L_z |\pm\Phi_\Lambda(0,\phi)\rangle + \frac{\hat{\boldsymbol{\phi}}}{R} \langle \pm\Phi_\Lambda(0,\phi)| L_y \sin\phi - L_x \cos\phi |\pm\Phi_\Lambda(0,\phi)\rangle .
\end{aligned} \qquad (6.12)$$

The gauge potential $\boldsymbol{A}(\boldsymbol{R})$ has been rotated into a body fixed orientation but given in terms of the Born-Oppenheimer eigenstates. As was stated in 3.1, the projection of the molecular electronic angular momentum along the internuclear axis is given by $L_{z'}$. Since we have managed to transform $\boldsymbol{A}(\boldsymbol{R})$ into an arbitrary orientation but given in terms of wavefunctions relative to $\hat{\mathbf{z}}$, we have from (3.8)

$$L_z |\pm\Phi_\Lambda(0,\phi)\rangle = \pm\Lambda |\pm\Phi_\Lambda(0,\phi)\rangle . \qquad (6.13)$$

Terms can be eliminated in (6.12) by using the raising/lowering operators on the Born-Oppenheimer states. The operators L_x and L_y can be given in terms of raising/lowering operators as [35]

$$L_x = \frac{1}{\sqrt{2}}(L_+ + L_-) \quad \text{and} \quad L_x = \frac{1}{i\sqrt{2}}(L_+ - L_-). \qquad (6.14)$$

Using [35]

$$L_{\pm}\,|\pm\Phi_{\Lambda}(0,\phi)\rangle \propto |\pm\Phi_{\Lambda\pm1}(0,\phi)\rangle \tag{6.15}$$

we can see that the act of the rasing/lowering operators is change the state described by the quantum number Λ by ±1. However using the fact that the states are orthogonal and that the difference in quantum number between any two doublet states is given by $2|\Lambda|$ means that terms involving L_x and L_y in (6.12) can be eliminated.

This then reduces (6.12) to

$$\boldsymbol{A}(\boldsymbol{R})_{+} = i\,\hat{\mathbf{R}}\,\langle\pm\Phi_{\Lambda}(0,\phi)|\,\frac{\partial}{\partial R}\,|\pm\Phi_{\Lambda}(0,\phi)\rangle + \frac{\hat{\boldsymbol{\phi}}\,\Lambda\,(1-\cos\theta)}{R\sin\theta}. \tag{6.16}$$

The radial portion of $\boldsymbol{A}(\boldsymbol{R})$ can be removed through the gauge transformation (5.2).

$$\boldsymbol{A} \rightarrow \boldsymbol{A}' = U^{-1}\boldsymbol{A}U + i\,U^{-1}\boldsymbol{\nabla}U. \tag{6.17}$$

Let U, U^{-1} and $\boldsymbol{A}(\boldsymbol{R})$ be given by

$$U = \exp\left[i\int^{R}\boldsymbol{A}(\boldsymbol{R}')\cdot d\boldsymbol{R'}\right],\ U^{-1} = \exp\left[-i\int^{R}\boldsymbol{A}(\boldsymbol{R}')\cdot d\boldsymbol{R'}\right] \quad \text{and} \quad \boldsymbol{A}(\boldsymbol{R}) = i\,\hat{\mathbf{R}}\,f(R) \tag{6.18}$$

respectively.

Then

$$U^{-1}\boldsymbol{A}U = i\,\hat{\mathbf{R}}\,U^{-1}f(R)U \tag{6.19}$$

and $\boldsymbol{\nabla}_R\,U = i\,\boldsymbol{A}(\boldsymbol{R})\,U \rightarrow -\hat{\mathbf{R}}\,f(R)\,U$ so that

$$i\,U^{-1}\boldsymbol{\nabla}U = -i\,\hat{\mathbf{R}}\,U^{-1}f(R)\,U. \tag{6.20}$$

Adding (6.19) and (6.20) gives zero and the radial portion of the vector potential has been gauged away. Thus (6.16) becomes

$$\boldsymbol{A}(\boldsymbol{R})_{+} = \frac{\hat{\boldsymbol{\phi}}\,\Lambda\,(1-\cos\theta)}{R\sin\theta}. \tag{6.21}$$

A similar calculation for R_- will show that

$$\boldsymbol{A}(\boldsymbol{R})_{-} = \frac{\hat{\boldsymbol{\phi}}\,\Lambda\,(-1-\cos\theta)}{R\sin\theta}. \tag{6.22}$$

Taking the curl of $\boldsymbol{A}(\boldsymbol{R})_+$ and $\boldsymbol{A}(\boldsymbol{R})_-$ in the respective regions gives a magnetic monopole of strength $|\Lambda|$

$$\boldsymbol{\nabla} \times \boldsymbol{A}_\pm = \boldsymbol{B} = \Lambda\,\frac{\hat{\mathbf{R}}}{R^2}. \tag{6.23}$$

This is the key result from our analysis. We have shown the vector potential that arises from the adiabatic coupling of electronic and nuclear motion in the modern Born-Oppenheimer approximation, given by (5.23) is non-trivial. We were not able to gauge the potential away and taking the curl of this potential gives a non-zero magnetic field. We will see in the Chapter 7 that this gauge potential is the same as that from a Dirac or a Wu and Yang monopole. In Chapter 8 we will show that this vector potential applied to the modern Born-Oppenheimer approximation gives the same Hamiltonian as that described by the traditional method.

Chapter 7

MAGNETIC MONOPOLES

Magnetic monopoles had been discussed in a classical context before Dirac's 1931 paper, notably by Poincaré [42, 46]. In 1931 Dirac published the first paper on magnetic monopoles in quantum theory. In his paper monopoles were thought of point charges like an electric charge, however there was one significant difference. Unlike a point electric charge, there is a singularity along the semi-infinite z axis which can be described as an infinitely thin solenoid that has the property of returning a magnetic flux to the monopole so that the total magnetic flux is zero. This singularity is known as the Dirac string. This extra piece satisfies Maxwell's equation $\boldsymbol{\nabla} \cdot \boldsymbol{B} = 0$. The presence of the string was reconciled by allowing it to be rotated to any other position with the assumption being made that all possible configurations were equally likely. This led to the string as being seen as an unphysical construct and the magnetic field of the string as not real [46, 51]. However in the Wu and Yang monopole formalism,[53, 60] they allow the magnetic monopole to have a magnetic flux of $4\pi g$ where g is the charge of the monopole. We will call Wu and Yang as Wu-Yang. In the introduction to Dirac's 1931 paper he comments on how the advancement of physical theories would need to rely on the advancement of mathematical progress and the ability to relate the two. This indeed turned out to be the case in this very paper as the mathematics of differential geometry progressed and connections were made between gauge theories and differential geometry. In the field of magnetic monopoles, Wu-Yang made this connection in a series of papers [53–59].

7.1 DIRAC MONOPOLES

As was discussed earlier, Maxwell's equations tell us that the divergence of the magnetic field is zero, or $\boldsymbol{\nabla} \cdot \boldsymbol{B} = 0$. If the assumption is made that magnetic monopoles exist, then it is expected that they will behave like a point charge with a "Coulombic" magnetic field. The magnetic field of a monopole is then given by

$$\boldsymbol{B} = g\frac{\hat{\mathbf{R}}}{R^2} \tag{7.1}$$

which satisfies $\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A}$ so that $\boldsymbol{\nabla} \cdot \boldsymbol{\nabla} \times \boldsymbol{A} = 0$. This holds as long as the origin is excluded but it is singular at $R = 0$. Using the divergence theorem, we have

$$\int_V \boldsymbol{\nabla} \cdot \boldsymbol{B} = \int_V \boldsymbol{\nabla} \cdot g \frac{\hat{\mathbf{R}}}{R^2} = g \oint_S \frac{\hat{\mathbf{R}}}{R^2} \cdot d\boldsymbol{\sigma} = 4\pi g = \Phi_m. \tag{7.2}$$

This then means that $\boldsymbol{\nabla} \cdot \boldsymbol{B} = 4\,\pi\, g\, \delta^3(\boldsymbol{R})$ which is a contradiction to the divergenceless magnetic field given by Maxwell's equation. It is Dirac's string that reconciles this by allowing for a return magnetic flux along an infinitely thin solenoid into the monopole so that the net flux out of the monopole is zero [18, 19]. Dirac defines the vector potential of a monopole in spherical coordinates as being given by [18]

$$\boldsymbol{A} = \frac{g}{2R} \tan \frac{\theta}{2} \hat{\boldsymbol{\phi}}. \tag{7.3}$$

or more commonly seen in modern writings by the trigonometrically equivalent forms [28, 36]

$$\begin{aligned} \boldsymbol{A} &= \frac{g}{R} \frac{(1 - \cos\theta)}{\sin\theta} \hat{\boldsymbol{\phi}} \quad \text{or,} \\ \boldsymbol{A} &= \frac{g}{R} \frac{\sin\theta}{(1 + \cos\theta)} \hat{\boldsymbol{\phi}}. \end{aligned} \tag{7.4}$$

As was discussed in the previous chapter, the vector potential is the gradient of the gauge function, and in this case the vector potential can be written as [46]

$$\boldsymbol{A} = -g(1 + \cos\theta) \boldsymbol{\nabla} \phi = (1 + \cos\theta) U^{-1} \boldsymbol{\nabla} U \quad \text{where} \quad U = e^{-i\,g\,\phi}. \tag{7.5}$$

There is a problem in this definition of the vector potential as it is singular along the negative z-axis. As such, we will denote $\boldsymbol{A}$ as $\boldsymbol{A}_+$ to mean an exclusion of the negative z-axis. Taking the curl of this equation over all space excluding the negative z-axis gives

$$\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A}_+ = g \frac{\hat{\mathbf{R}}}{R^2}. \tag{7.6}$$

The middle term satisfies the condition that $\boldsymbol{\nabla} \cdot \boldsymbol{\nabla} \times \mathbf{A}_+ = 0$ but the right hand term is given by $\boldsymbol{\nabla} \cdot \boldsymbol{B} = 4\pi g \delta^3(\boldsymbol{R})$. Because the vector potential has a singularity along the along the negative z-axis, it is a distribution and as such the curl of $\boldsymbol{A}_+$ is correctly given by [6, 51]

$$\boldsymbol{\nabla} \times \boldsymbol{A}_+ = g \frac{\hat{\mathbf{R}}}{R^2} + 4\pi\, g\, \Theta(-z) \delta(x) \delta(y) \hat{\mathbf{k}} \tag{7.7}$$

where $\Theta(z)$ is the unit step function defined by $\Theta(z) = 1$ for $z > 0$ and $\Theta(z) = 0$ for $z < 0$. The condition satisfying Maxwell's equation has now been met that

$$\boldsymbol{\nabla} \cdot \boldsymbol{B} = \boldsymbol{\nabla} \cdot \boldsymbol{\nabla} \times \boldsymbol{A}_+ = 0 \tag{7.8}$$

which gives

$$\Phi = \int \boldsymbol{B} \cdot d\boldsymbol{\sigma} = \int g \frac{\hat{\mathbf{R}}}{R^2} \cdot d\boldsymbol{\sigma} + \int 4\pi g \Theta(-z)\delta(x)\delta(y)\hat{\mathbf{k}} \cdot d\boldsymbol{\sigma} = 4\pi g - 4\pi g = 0 \tag{7.9}$$

and the magnetic field is now fluxless and Maxwell's equation is satisfied.

As was discussed in the previous section the vector potential is not unique and can be transformed as

$$\boldsymbol{A}_+ \to \boldsymbol{A}_+ + iU^{-1}\boldsymbol{\nabla} U = \boldsymbol{A}_+ \pm \boldsymbol{\nabla}\lambda \tag{7.10}$$

depending on the sign of the gauge function. This allows the string singularity to be rotated to another position. An example of this is the gauge $U = e^{2i\mu\phi}$ with the gauge function being given by $\lambda = 2g\phi$. Substituting this into (7.10) we get

$$\boldsymbol{A}_+ \to \ \boldsymbol{A}_- = \boldsymbol{A}_+ - \boldsymbol{\nabla} 2g\phi = \frac{g}{r}\frac{(1-\cos\theta)}{\sin\theta}\hat{\boldsymbol{\phi}} - \frac{2g}{R\sin\theta}\hat{\boldsymbol{\phi}} = \frac{g}{R}\frac{(-1-\cos\theta)}{\sin\theta}\hat{\boldsymbol{\phi}}. \tag{7.11}$$

This now describes a vector potential that is singular along the positive z-axis. Taking the curl of this equation gives

$$\boldsymbol{\nabla} \times \boldsymbol{A}_- = g\frac{\hat{\mathbf{R}}}{R^2} - 4\pi g \Theta(z)\delta(x)\delta(y)\hat{\mathbf{k}}. \tag{7.12}$$

A similar calculation to the one done above shows that integrating this vector potential again leads to a fluxless magnetic field.

The discussion above shows that there is no global vector potential that uniquely describes the magnetic field of a monopole and two different vector potentials are required to give a magnetic monopole. Dirac explained the rotational invariance of the string by using "Dirac's veto" which states that the trajectory of an electrically charged particle must never cross the string, i.e. its wavefunction vanishes there [18, 19, 23].

There is another gauge transformation that can be used which splits the string singularity into two strings and as such the vector potential is singular along the entire z-axis. This gauge was due to Schwinger [45] who thought it was better suited to quantum field theory [46, 60].

Consider the gauge $U = e^{i\Lambda\phi}$. Then

$$\boldsymbol{A}_+ \rightarrow \ \boldsymbol{A}_\pm = \boldsymbol{A}_+ - \boldsymbol{\nabla} g\phi = \frac{g}{R}\frac{(1-\cos\theta)}{\sin\theta}\hat{\boldsymbol{\phi}} - \frac{g}{R\sin\theta}\hat{\boldsymbol{\phi}} = -\frac{g}{R}\frac{\cos\theta}{\sin\theta}\hat{\boldsymbol{\phi}}. \tag{7.13}$$

7.2 WU-YANG MONOPOLES

In the Wu-Yang version of magnetic monopoles [53, 54, 56, 56–59], a different mathematical approach (possibly even more physically realistic) is employed in order to remove the string of singularities that plagued the Dirac version of monopoles. Wu and Yang were able to make the connection between the physics of gauge fields and the mathematics of differential geometry. This advancement in mathematics and it's connection to physics is exactly what Dirac had predicted would be needed in order to explain more phenomena [18].

The Wu-Yang formalism to describe the the magnetic monopole is to reconsider the idea of the wavefunction and instead consider it a wave section [53]. Instead of trying to consider one wavefunction to describe the monopole, the space surrounding it is divided into two sections. Each section has a differing wave section for the monopole, but in a region of overlap between these two sections they are related through a gauge transformation. The space that a given section occupies is singularity free. Thus instead of trying to find one vector potential for the entire monopole, one is found in each section, the curl of which gives the correct description for the magnetic field of a monopole. Starting again with the magnetic field of the monopole given by

$$\boldsymbol{B} = \frac{g}{R^2}\hat{\mathbf{R}} \tag{7.14}$$

and it's divergence $\boldsymbol{\nabla}\cdot\boldsymbol{B} = 4\pi g\delta^3(\boldsymbol{R})$. We have the same situation described in the discussion on Dirac monopoles where the monopole has a flux of $\Phi_m = 4\pi g$. In the Wu-Yang version of the monopole, Yang states that the correct version of the monopole does have a flux, and is not fluxless as described by Maxwell's equations [51, 59, 60].

In order to arrive at this condition for the monopole, the space surrounding it is divided into two spaces, each a semi-spherical surface with a common region of overlap. The vector potentials given in each region are defined by

$$\boldsymbol{A}_+ = \left[\frac{g\,(1-\cos\theta)}{R\sin\theta}\right]\hat{\boldsymbol{\phi}} \quad \text{and} \quad \boldsymbol{A}_- = \left[\frac{g\,(-1-\cos\theta)}{R\sin\theta}\right]\hat{\boldsymbol{\phi}} \tag{7.15}$$

where the sections are given by

$$\begin{aligned}\boldsymbol{A}_+ \quad &\in \quad 0 \leq \theta < \pi - \epsilon, \\ \boldsymbol{A}_- \quad &\in \quad \epsilon < \theta \leq \pi. \end{aligned} \tag{7.16}$$

The two surfaces overlap where $\epsilon < \theta < \pi - \epsilon$ which can be minimized with the overlap along the equator of $\pi/2 - \delta < \theta < \pi/2 + \delta$ and θ is the polar angle. It is to be noted that these are the same vector potentials that are described in the previous section under Dirac's monopole. As such you get the flux that you would expect from a point magnetic charge without a string of returning magnetic flux. The total flux through a surface is then

$$\int \boldsymbol{B} \cdot d\boldsymbol{\sigma} = \int \boldsymbol{\nabla} \times \boldsymbol{A} \cdot d\boldsymbol{\sigma} = \int \boldsymbol{\nabla} \times \boldsymbol{A}_+ \cdot d\boldsymbol{\sigma}_+ + \boldsymbol{\nabla} \times \boldsymbol{A}_- \cdot d\boldsymbol{\sigma}_- = 4\pi g \tag{7.17}$$

where the vector potential has been split into it's two components and integrated over the respective surface. An application of Stokes' Theorem gives

$$\int \boldsymbol{\nabla} \times \boldsymbol{A}_+ \cdot d\boldsymbol{\sigma}_+ + \boldsymbol{\nabla} \times \boldsymbol{A}_- \cdot d\boldsymbol{\sigma}_- = \oint_C \boldsymbol{A}_+ \cdot d\mathbf{l}_+ + \boldsymbol{A}_- \cdot d\mathbf{l}_- = 4\pi g \tag{7.18}$$

where C is the closed curve bordering the surface. The standard orientation convention is observed so the right hand rule determines the direction of the outward normal. As such the upper and lower surfaces integrate in opposite directions. Thus the $d\boldsymbol{l}$'s of the two surfaces are of opposite sign and we can rewrite the above equation as

$$\oint_C (\mathbf{A}_+ - \boldsymbol{A}_-) \cdot d\boldsymbol{l}_+ = 4\pi g \tag{7.19}$$

by the assumption that the flux is non-zero. Since the same curve is being integrated over with different vector potentials, a gauge transformation is needed between $\boldsymbol{A}_+$ and $\boldsymbol{A}_-$ along the overlap. This can be given by,

$$\boldsymbol{A}_+ \to \boldsymbol{A}_- = \boldsymbol{A}_+ + i\,U^{-1}\boldsymbol{\nabla} U \tag{7.20}$$

where $U = e^{2i\,\Lambda\,\phi}$ is the gauge and the transition function is given by $\lambda(\mathbf{r}) = 2i\mu\phi$. Inserting this into (7.20) gives

$$\boldsymbol{A}_{+} \rightarrow\ \boldsymbol{A}_{-} = \boldsymbol{A}_{+} - \boldsymbol{\nabla} 2g\phi = \frac{g}{R}\frac{(-1-\cos\theta)}{\sin\theta}\hat{\boldsymbol{\phi}}. \tag{7.21}$$

It is to be noted that this is exactly the same gauge transformation that rotates the Dirac string around the monopole.

The wave sections must also be related through a gauge transformation that is given by

$$\psi_{+}(\boldsymbol{R}) = \psi_{-}(\boldsymbol{R})e^{2i\,\Lambda\,\phi}. \tag{7.22}$$

This ensures that the wave sections describe a uniform magnetic field over the entire space surrounding the monopole.

7.3 NON-INTEGRABILITY OF PHASE AND MAGNETIC MONOPOLE QUANTIZATION

In Dirac's seminal papers on magnetic monopoles, he considered the quantum effect of a charged particle in the presence of an electromagnetic potential and how this effected the wavefunction in (5.1) [18, 19]. If there is no electromagnetic potential present, then the transportation of the wavefunction about a closed path is unchanged and [14]

$$F(0) = F(2\pi). \tag{7.23}$$

Dirac noted that the phase of the wavefunction of a charged particle can change in the presence of a potential and that the phase of the wavefunction under transport can be written as [18, 46]

$$F(\boldsymbol{R}) = F_0(\boldsymbol{R})e^{i\,e\int^{\mathbf{R}}\mathbf{A}(\mathbf{R}')\cdot d\mathbf{R}'} \tag{7.24}$$

where $F_0(\boldsymbol{R})$ is the wavefunction of a free particle. From (5.12) the vector potential is proportional to the gradient of the gauge function which means that the gauge function is the line integral of $\boldsymbol{A(R)}$. Dirac noted that this change in phase need not be zero, however the change in phase around a closed path in the presence of a magnetic monopole must be an integer multiple of 2π in order that the wavefunction maintains single-valuedness. This can be shown by [46]

$$e \oint \boldsymbol{A(R')} \cdot d\boldsymbol{R'} = 2\pi\, n. \tag{7.25}$$

This integral is also recognized as the flux of a magnetic field through a surface, σ. This gives

$$e \oint \boldsymbol{A(R')} \cdot d\boldsymbol{R'} = e \int_\sigma d\sigma \cdot \boldsymbol{B} = 4\pi e\, g. \tag{7.26}$$

This gives

$$2\pi\, n = 4\pi e\, g \quad \text{or} \quad g = \frac{n}{2\, e}. \tag{7.27}$$

This condition holds in the case of a Dirac string [18]. In a general vector potential this restriction on single valuedness is not required and the flux through a closed loop is given by [14]

$$F(2\pi) = F_0(0) e^{i4\pi e\, g}. \tag{7.28}$$

Chapter 8

COMPARISON OF TRADITIONAL QUANTUM DESCRIPTION AND GAUGE THEORETIC TREATMENT

Now that we have shown that the potentials appearing in the Schrödinger equation for nuclear motion are gauge fields, we are in a position to compare the equality of the Hamiltonians appearing in (3.24) and (5.19). Our analysis in section 8.2 will show that the non-adiabatic correction terms appearing in the traditional Born-Oppenheimer approximation arise from gauge fields.

Substituting the definition of the gauge covariant derivative into the nuclear Hamiltonian gives

$$-\frac{1}{2\mu}\big[\boldsymbol{\nabla}_R - i\,e\,\boldsymbol{A}(\boldsymbol{R})\big]^2 + e\,\tilde{\epsilon}(R) = -\frac{1}{2\mu}\boldsymbol{D}^2 + e\,\tilde{\epsilon}(R) \tag{8.1}$$

and there are two different approaches to solving the nuclear Schrödinger equation for each side of (8.1). We will sketch these approaches below.

8.1 MAGNETIC MONOPOLE ANGULAR MOMENTUM

In the presence of a magnetic monopole, the angular momentum vector of a charged particle needs to modified in order that the angular momentum is a integral of the motion, that is [30, 46]

$$\frac{d\tilde{\boldsymbol{L}}}{dt} = 0 \tag{8.2}$$

where $\tilde{\boldsymbol{L}}$ is the generalized angular momentum. This was first considered by Poincaré and Thomson [42, 48] Take a magnetic monopole to be located at the origin and a charged particle of strength e located at the point $\boldsymbol{r'}$. The magnetic and electric fields at the point $\boldsymbol{r}$ are given by

$$\boldsymbol{B} = g\frac{\hat{\mathbf{r}}}{r^2} \quad \text{and} \quad \boldsymbol{E} = e\frac{\boldsymbol{r}-\boldsymbol{r'}}{|\boldsymbol{r}-\boldsymbol{r'}|^3} \tag{8.3}$$

respectively. In order for (8.2) to hold, there needs to be a modification to the standard angular momentum given by

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}. \tag{8.4}$$

The modification Thomson made was to integrate the cross product of the position vector with the Poynting vector to generate an angular momentum of the electromagnetic field.

$$\tilde{\boldsymbol{L}} = \int \boldsymbol{r} \times \big(\boldsymbol{E} \times \boldsymbol{B}\big) d\tau = -e\, g\, \hat{\mathbf{r}}. \tag{8.5}$$

The details to the solution of this integral can be found in [26].

The generalized angular momentum of a charged particle in the presence of a magnetic monopole can then be given by

$$\tilde{\boldsymbol{L}} = (\boldsymbol{r} \times \boldsymbol{p}) - e\, g\, \hat{\mathbf{r}} = \boldsymbol{L} - e\, g\, \hat{\mathbf{r}}. \tag{8.6}$$

In our case, we have the momentum operator as given by the gauge covariant derivative, $\boldsymbol{D}$. Similarly we have [5, 15, 37, 46, 61]

$$\tilde{\boldsymbol{J}} = -i(\,\boldsymbol{R} \times \boldsymbol{D}) - e\, g\, \hat{\mathbf{R}} \tag{8.7}$$

which has the following commutation relations [15]:

$$\begin{aligned}
[\tilde{J}_j, D_k] &= i\, \epsilon_{jkl}\, D_l, \\
[\tilde{J}_j, R_k] &= i\, \epsilon_{jkl}\, R_l, \\
[\tilde{J}_j, J_k] &= i\, \epsilon_{jkl}\, \tilde{J}_l, \\
[\tilde{J}_j, H] &= 0,
\end{aligned} \tag{8.8}$$

where H is the Hamiltonian of the gauge covariant Born-Oppenheimer approximation (5.19). These are the standard commutation relations for a spherically symmetric system [47]. In this form it is easy to show now that the angular momentum commutes with Hamiltonian of the diatom (5.19).

$$\begin{aligned}
[\tilde{J}_i, H] &= \frac{1}{2\mu}[\tilde{J}_i, \boldsymbol{D} \cdot \boldsymbol{D}] + [\tilde{J}_i, \tilde{\epsilon}(R)] \\
&= \frac{1}{2\mu}[\tilde{J}_j, D_j D_j] = 0
\end{aligned} \tag{8.9}$$

upon applying the first of the relations in (8.8).

8.1.1 METHOD USING GAUGE COVARIANT DERIVATIVE

Using the identity [15]

$$\boldsymbol{D} \cdot \boldsymbol{D} = (\boldsymbol{D} \cdot \boldsymbol{R}) \frac{1}{R^2} (\boldsymbol{R} \cdot \boldsymbol{D}) - (\boldsymbol{D} \times \boldsymbol{R}) \frac{1}{R^2} (\boldsymbol{R} \times \boldsymbol{D}). \tag{8.10}$$

Using the commutation relations found is section 5.4, the first term is

$$(\boldsymbol{D} \cdot \boldsymbol{R}) \frac{1}{R^2} (\boldsymbol{R} \cdot \boldsymbol{D}) = \frac{1}{R^2} \frac{\partial}{\partial R} \Big(R^2 \frac{\partial}{\partial R} \Big).. \tag{8.11}$$

The second term can be rewritten as

$$-(\boldsymbol{D} \times \boldsymbol{R}) \frac{1}{R^2} (\boldsymbol{R} \times \boldsymbol{D}) = \frac{1}{R^2} (\boldsymbol{R} \times \boldsymbol{D})^2. \tag{8.12}$$

Inserting (8.11) and (8.12) into (8.10) gives

$$\boldsymbol{D} \cdot \boldsymbol{D} = \frac{1}{R^2} \frac{\partial}{\partial R} \Big(R^2 \frac{\partial}{\partial R} \Big) + \frac{1}{R^2} (\boldsymbol{R} \times \boldsymbol{D})^2. \tag{8.13}$$

From (8.7) we see that

$$\tilde{\boldsymbol{J}}^2 = -(\boldsymbol{R} \times \boldsymbol{D})^2 + e^2 g^2 \tag{8.14}$$

which can rearranged to give

$$(\boldsymbol{R} \times \boldsymbol{D})^2 = -\tilde{\boldsymbol{J}}^2 + e^2 g^2. \tag{8.15}$$

Inserting (8.15) into (8.13) gives

$$\boldsymbol{D} \cdot \boldsymbol{D} = \frac{1}{R^2} \frac{\partial}{\partial R} \Big(R^2 \frac{\partial}{\partial R} \Big) - \frac{\tilde{\boldsymbol{J}}^2 + e^2 g^2}{R^2}. \tag{8.16}$$

This can be inserted into the right side of the Hamiltonian of (8.1) giving

$$H = -\frac{1}{2\mu R^2} \left[\frac{\partial}{\partial R} \Big(R^2 \frac{\partial}{\partial R} \Big) + \frac{\tilde{\boldsymbol{J}}^2 - e^2 g^2}{R^2} \right] = -\frac{1}{2\mu R^2} \left[\frac{\partial}{\partial R} \Big(R^2 \frac{\partial}{\partial R} \Big) - \frac{J(J+1) - e^2 g^2}{R^2} \right]. \tag{8.17}$$

The third term is expanded on a subspace of states of given total angular momentum [15]. This is seen to be equivalent to the first the terms of (4.1) which describes the Hamiltonian governing the nuclear motion of the diatom. A comparison of these Hamiltonians shows that $\Lambda^2 = e^2 g^2$, and so the angular momentum projection of the electrons along the axis of the diatom is akin to the angular momentum of the electromagnetic field, the second term in (8.7). The ϕ dependence shows up as the $e\,g$ term in the Hamiltonian and the solutions are given by the Wigner function [15], $d^J_{M,\Lambda}(\theta)$ where $J = |e\,g|, |e\,g|+1, |e\,g|+2, \ldots$

8.1.2 METHOD USING THE GAUGE POTENTIAL

We will be inserting the gauge potential of (7.13) into the left side of the Hamiltonian (8.1), where

$$\big[\boldsymbol{\nabla}_R - i\,e\,\boldsymbol{A}(\boldsymbol{R})\big]^2 = \nabla^2_R - i\,e\,\boldsymbol{\nabla}_R \cdot \boldsymbol{A}(\boldsymbol{R}) - 2i\,e\,\boldsymbol{A}\cdot\boldsymbol{\nabla}_R - e^2\,\boldsymbol{A}(\boldsymbol{R})\cdot\boldsymbol{A}(\boldsymbol{R}). \tag{8.18}$$

and

$$\boldsymbol{A}(\boldsymbol{R}) = \frac{g}{R}\frac{\cos\theta}{\sin\theta}\hat{\boldsymbol{\phi}}. \tag{8.19}$$

Substituting (8.19) into (8.18) gives

$$\begin{aligned}\frac{1}{2\,\mu\,R^2}\big[\boldsymbol{\nabla}_R - i\boldsymbol{A}(\boldsymbol{R})\big]^2 =& \frac{1}{2\,\mu\,R^2}\Bigg[-\frac{\partial}{\partial R}\Big(R^2\frac{\partial}{\partial R}\Big) \\ &-\frac{1}{\sin^2\theta}\Bigg[\sin\theta\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial}{\partial\theta}\Big) + \Big(\frac{\partial}{\partial\phi} - i\Lambda\cos\theta\Big)^2\Bigg] + \Lambda^2\Bigg]\end{aligned} \tag{8.20}$$

where

$$\boldsymbol{J}^2 = -\frac{1}{\sin^2\theta}\Bigg[\sin\theta\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial}{\partial\theta}\Big) + \Big(\frac{\partial}{\partial\phi} - i\Lambda\cos\theta\Big)^2\Bigg]. \tag{8.21}$$

This is the same operator as (4.14) for rotation of the diatom. If we apply the angular wavefunction of (4.13) we obtain after rearranging

$$\big[\boldsymbol{\nabla}_R - i\boldsymbol{A}(\boldsymbol{R})\big]^2 = -\frac{1}{2\,\mu\,R^2}\Bigg[\frac{\partial}{\partial R}\Big(R^2\frac{\partial}{\partial R}\Big) - \frac{J(J+1)-\Lambda^2}{R^2}\Bigg]. \tag{8.22}$$

There is a problem with the analysis used above to get the same differential equation as the molecular symmetric top (4.14). The gauge potential given in (8.19) is singular at $\theta = 0, \pi$, however the solution to the differential equation, the Wigner d-function, $d^J_{M,\Lambda}$ is regular everywhere. If we choose a different gauge, namely the gauge used in the $\boldsymbol{A}_+$ region of the Wu-Yang monopole,

$$\boldsymbol{A}_{+} = \left[\frac{g(1-\cos\theta)}{R\sin\theta}\right]\hat{\boldsymbol{\phi}} \quad \text{where} \quad \boldsymbol{A}_{+} \quad \in \quad 0 \leq \theta < \pi - \epsilon. \tag{8.23}$$

Substituting this gauge potential into (8.18) gives in place of (8.20)

$$\begin{aligned}\frac{1}{2\,\mu\,R^2}\left[\boldsymbol{\nabla}_R - i\boldsymbol{A}(\boldsymbol{R})\right]^2 =& \frac{1}{2\,\mu\,R^2}\Bigg[-\frac{\partial}{\partial R}\Big(R^2\frac{\partial}{\partial R}\Big) \\ &- \frac{1}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial}{\partial\theta}\Big) + \Big(\frac{\partial}{\partial\phi} - i\Lambda(1-\cos\theta)\Big)^2\right] + \Lambda^2\Bigg].\end{aligned} \tag{8.24}$$

The solution to this equation is given by [4, 55]

$$Y^{\Lambda}_{JM}(\theta\phi) = e^{i(M+\Lambda)\phi}d^{J}_{M,-\Lambda}. \tag{8.25}$$

The gauge in (8.23) is regular everywhere in it's domain as is the solution in (8.25). Similarly applying the gauge

$$\boldsymbol{A}_{-} = \left[\frac{g(-1-\cos\theta)}{r\sin\theta}\right]\hat{\boldsymbol{\phi}} \quad \text{where} \quad \boldsymbol{A}_{-} \quad \in \quad \epsilon < \theta \leq \pi \tag{8.26}$$

Substituting this gauge potential into (8.18) gives in place of (8.20)

$$\begin{aligned}\frac{1}{2\,\mu\,R^2}\left[\boldsymbol{\nabla}_R - i\boldsymbol{A}(\boldsymbol{R})\right]^2 =& \frac{1}{2\,\mu\,R^2}\Bigg[-\frac{\partial}{\partial R}\Big(R^2\frac{\partial}{\partial R}\Big) \\ &- \frac{1}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial}{\partial\theta}\Big) + \Big(\frac{\partial}{\partial\phi} - i\Lambda(-1-\cos\theta)\Big)^2\right] + \Lambda^2\Bigg].\end{aligned} \tag{8.27}$$

The solution to this equation is given by [4, 55]

$$Y^{\Lambda}_{JM}(\theta\phi) = e^{i(M-\Lambda)\phi}d^{J}_{M,-\Lambda}. \tag{8.28}$$

The solutions given in (8.25) and (8.28) are called the monopole harmonics [55] As was described in Chapter 7.2, the gauge potentials are related through a gauge transformation in the regions of overlap. By applying the theory of gauge potentials, we see there are two solutions required to the nuclear Schrödinger equation so that the gauge potential is regular everywhere. This situation in not discussed in the traditional description of diatomic rotation given in (4.15).

8.2 CORRECTION TERMS

By using gauge theoretic methods we have obtained the angular momentum eigenvalues of the nuclei along with the projection of the angular momentum of the electrons along the internuclear axis. We will now show how the following two correction terms are derived.

$$\frac{\Omega^2(R)}{2\,\mu\,R^2} \quad \text{and} \quad \frac{B(R)}{2\mu}. \tag{8.29}$$

We first expand scalar correction of (5.31).

$$\frac{1}{2\,\mu}\sum_{k\neq 1}\boldsymbol{A}^{1k}\cdot\boldsymbol{A}^{k1} = \frac{1}{2\,\mu}\sum_{k\neq 1}\boldsymbol{A}_R^{1k}\cdot\boldsymbol{A}_R^{k1} + \frac{1}{2\,\mu R^2}\sum_{k\neq 1}\boldsymbol{A}_\theta^{1k}\cdot\boldsymbol{A}_\theta^{k1} + \frac{1}{2\,\mu R^2\sin^2\theta}\sum_{k\neq 1}\boldsymbol{A}_\phi^{1k}\cdot\boldsymbol{A}_\phi^{k1}. \tag{8.30}$$

Where the gauge potential is written in terms of the adiabatic eigenstates that were calculated in chapter 6.2. This gives for the gauge potential

$$\begin{aligned}\boldsymbol{A}^{1k}\cdot\boldsymbol{A}^{k1} =& i\,\hat{\mathbf{R}}\,\langle\Phi_1|\,\partial_R\,|\Phi_k\rangle - \frac{\hat{\boldsymbol{\theta}}}{R}\,\langle\Phi_1|\cos\phi\,L_{y'} - \sin\phi\,L_{x'}\,|\Phi_k\rangle\\ &- \frac{\hat{\boldsymbol{\phi}}}{R\,\sin\theta}\,\langle\Phi_1|\,(\cos\theta-1)\,L_{z'} - \sin\theta\cos\phi\,L_{x'} - \sin\theta\sin\phi\,L_{y'}\,|\Phi_k\rangle\,.\end{aligned} \tag{8.31}$$

We now expand each of the terms in (8.31).

$$\frac{1}{2\,\mu}\boldsymbol{A}_R^{1k}\cdot\boldsymbol{A}_R^{k1} = -\frac{1}{2\,\mu}\,\langle\Phi_1|\,\partial R\,|\Phi_k\rangle\cdot\langle\Phi_k|\,\partial R\,|\Phi_1\rangle\,. \tag{8.32}$$

Using

$$\big(\,\langle\Phi_1|\,\partial_R\big)\,|\Phi_k\rangle = -\,\langle\Phi_1|\,\big(\partial_R\,|\Phi_k\rangle\,\big) \tag{8.33}$$

gives [61]

$$\frac{1}{2\,\mu}\boldsymbol{A}_R^{1k}\cdot\boldsymbol{A}_R^{k1} = \frac{1}{2\,\mu}\big|\,\langle\Phi_1|\,\partial R\,|\Phi_k\rangle\,\big|^2. \tag{8.34}$$

which is equivalent to $B(R)$ in (3.10). The angular components of (8.30) are:

$$\frac{1}{2\,\mu R^2}\boldsymbol{A}_\theta^{1k}\cdot\boldsymbol{A}_\theta^{k1} = \frac{1}{2\,\mu R^2}\,\langle\Phi_1|\cos^2\phi\,L_{z'}^2 - \cos\phi\sin\phi\,\{L_{x'},L_{y'}\} + \sin^2\phi\,L_{y'}^2\,|\Phi_k\rangle\,, \tag{8.35}$$

$$\begin{aligned}\frac{1}{2\,\mu R^2\sin^2\theta}\boldsymbol{A}_\phi^{1k}\cdot\boldsymbol{A}_\phi^{k1} =& \frac{1}{2\,\mu R^2\sin^2\theta}\langle\Phi_1|\,(\cos\theta-1)\,L_{z'}^2+\sin^2\theta\cos^2\phi\,L_{x'}^2+\sin^2\theta\sin^2\phi\,L_{y'}^2\\ &-(\cos\theta-1)\sin\theta\cos\phi\,\{L_{x'},L_{z'}\}-(\cos\theta-1)\sin\theta\sin\phi\,\{L_{y'},L_{z'}\}\\ &+\sin^2\theta\sin\phi\cos\phi\{L_{x'},L_{y'}\}\,|\phi_k\rangle \qquad (8.36)\end{aligned}$$

where $\{L_{j'},L_{k'}\}$ is the anti-commutator of two operators and (8.33) was used. Combining (2.6), (2.7) and (2.8), using the fact that $\langle\Phi_1|\,L_{z'}\,|\Phi_k\rangle=0$ for $1\neq k$ since $L_{z'}$ is diagonal, and simplifying then (2.3) becomes

$$\frac{1}{2\,\mu}\sum_{k\neq 1}\boldsymbol{A}^{1k}\cdot\boldsymbol{A}^{k1}=\frac{1}{2\,\mu}\langle\Phi_1|\,L_{x'}^2+L_{y'}^2\,|\Phi_2\rangle \qquad (8.37)$$

which is equivalent to $\Omega^2(R)$ in (3.20). We have shown that by using a gauge theoretic treatment, that the traditional terms describing rovibrational motion in diatoms can be recreated.

8.3 LORENTZ FORCE

In Chapter 2 of the traditional Born-Oppenheimer approximation, a Hellman-Feynman force was related to the scalar potential governing nuclear motion as in (2.44) [24]. In the gauge covariant Born-Oppenheimer approximation [37, 61, 64], it has been shown that a Lorentz type force, or an induced effective "magnetic force" can appear [2, 61, 62, 64].

Ehrenfest's theorem describes how the expectation values of the position and momentum of a particle change with time [47]. First find the expectation value of the position

$$\frac{d\langle\boldsymbol{R}\rangle}{dt}=-i\big\langle[\boldsymbol{R},H]\big\rangle+\Big\langle\frac{\partial\boldsymbol{R}}{\partial t}\Big\rangle \qquad (8.38)$$

where

$$H=-\frac{1}{2\mu}\boldsymbol{D}\cdot\boldsymbol{D}+\tilde{\epsilon}(R). \qquad (8.39)$$

$\boldsymbol{R}$ is not a function of time so that the second term on the right of (8.38) is zero. Using the gauge covariant form of the Born-Oppenheimer equation from (8.39) and substituting this into (8.38)

$$-i\langle[R_j,H]\rangle=\frac{i}{2\,\mu}\Big\langle[R_j,\boldsymbol{D}\cdot\boldsymbol{D}]\Big\rangle-i\,\Big\langle[R_j,\tilde{\epsilon}(R)]\Big\rangle. \qquad (8.40)$$

The third term is zero since scalars commute and taking the j^{th} term of R and expanding out gives.

$$\frac{d\langle R_j\rangle}{dt} = \frac{i}{2\,\mu}\sum_k \Big(\big\langle D_k\,[R_j, D_k]\big\rangle + \big\langle [R_j, D_k]\,D_k\big\rangle\Big). \tag{8.41}$$

Using (5.18) gives

$$\frac{d\langle R_j\rangle}{dt} = \frac{\langle D_j\rangle}{\mu} \quad \text{or} \quad \frac{d\langle \boldsymbol{R}\rangle}{dt} = \frac{\langle \boldsymbol{D}\rangle}{\mu}. \tag{8.42}$$

From (5.15), $\boldsymbol{D}$ is $-i$ times the kinematical momentum. So the expectation value of the position with respect to time gives a momentum divided by a mass, which is equivalent to a velocity. To find the expectation value of the velocity we have

$$\frac{d\langle \boldsymbol{D}\rangle}{dt} = -i\big\langle[\boldsymbol{D}, H]\big\rangle + \Big\langle\frac{\partial \boldsymbol{D}}{\partial t}\Big\rangle \tag{8.43}$$

where H is given by (8.39). Choosing the j^th component

$$\frac{d\langle D_j\rangle}{dt} = \frac{i}{2\,\mu}\Big\langle[D_j, \boldsymbol{D}\cdot\boldsymbol{D}]\Big\rangle - i\,\Big\langle[D_j, \tilde{\epsilon}(R)]\Big\rangle + \Big\langle\frac{\partial D_j}{\partial t}\Big\rangle. \tag{8.44}$$

$\boldsymbol{D}$ is not a function of time so the last term in (8.44) is zero. Expanding this out gives

$$\frac{d\langle D_j\rangle}{dt} = \frac{i}{2\,\mu}\sum_k \Big(\big\langle D_k\,[D_j, D_k] + [D_j, D_k]\,D_k\big\rangle\Big) - i\,\Big\langle[\partial_j - i\,e\,A_j, \tilde{\epsilon}(R)]\Big\rangle. \tag{8.45}$$

Using (5.17), $[D_j, D_k] = -i\,e\,\epsilon_{jkl}\,B_l$ and (5.18), (8.45) becomes

$$\frac{d\langle D_j\rangle}{dt} = \frac{(i)(-i)}{2\,\mu}\sum_k\sum_l \epsilon_{jkl}\,\Big(\big\langle D_k\,B_l + B_l\,D_k\big\rangle\Big) - i\,(-i)\,\Big\langle[\partial_j, \tilde{\epsilon}(R)]\Big\rangle. \tag{8.46}$$

Applying the Levi-Civita symbol the term in brackets can be written as

$$\epsilon_{jkl}\,\Big(\big\langle D_k\,B_l + B_l\,D_k\big\rangle\Big) = \epsilon_{jkl}\,\Big(\big\langle D_k\,B_l - B_k\,D_l\big\rangle\Big). \tag{8.47}$$

We can see that these represent cross product terms and thus (8.47) represents the expectation value as

$$\frac{d\langle \boldsymbol{D}\rangle}{dt} = \frac{1}{2}\big\langle \boldsymbol{v}\times\boldsymbol{B} - \boldsymbol{B}\times\boldsymbol{v}\big\rangle - \boldsymbol{\nabla}_R\big\langle\tilde{\epsilon}(R)\big\rangle. \tag{8.48}$$

where we have used $\frac{\boldsymbol{D}}{\mu} = \boldsymbol{v}$. The application of Ehrenfest's theorem to the gauge covariant Born-Oppenheimer approximation has led to a Lorentz type force as well as the Hellman-

Feynman force that appeared in the traditional Born-Oppenheimer approximation.

8.4 CONCLUSIONS

We have treated the Born-Oppenheimer approximation for molecular motion with non-adiabatic coupling through the application of gauge theory. All terms in the Hamiltonian describing nuclear motion that arise from non-adiabatic coupling in the traditional approach to molecular dynamics appear in a gauge theoretic framework. In place of applying differential operators to the electronic wavefunctions to derive the nuclear Hamiltonian, a unitary operator is applied to the electronic wavefunctions giving rise to a gauge potential. This allows the Hamiltonian for the nuclear motion to be cast in a gauge covariant form. The gauge covariant treatment shows how an effective magnetic monopole appears in a rotating diatom giving rise to a Lorentz type force. An unexplored problem that arises in the gauge theoretic treatment is that two wave section solutions, which are related through a gauge transformation, are required to describe the nuclear angular motion through all arbitrary angles in order to deal with the monopole singularity. This situation is not discussed in traditional molecular dynamics.

We feel that the gauge theoretic treatment of rovibrational motion in diatoms is an advancement over the traditional techniques.

Firstly, the mathematical calculations to derive the non-adiabatic coupling terms are more straightforward than the traditional approach. Secondly, gauge theory is used to describe our current understanding of interactions among elementary particles, and in the context of this thesis, appears to explain molecular interactions also. In the introduction to Dirac's 1931 paper, he presciently comments on how the advancement of physical theories would need to rely on the advancement of mathematical progress and the ability to relate the two. This was the case for Wu and Yang's magnetic monopole and we posit that this is also the case for a gauge theoretic approach to molecular dynamics. The adoption of gauge theory to describe diatomic motion can be compared to a quote from Feynman [25] in 1963 where he is describing the Aharonov-Bohm effect, "It is interesting that something like this can be around for thirty years but, because of certain prejudices of what is and is not significant, continues to be ignored."

Appendix A

PERTURBATION OF THE MORSE POTENTIAL

We consider $H = H^{(0)} + H^{(1)}$ where $H^{(0)} = D\beta^2(R - R_e)^2$ and $H^{(1)} = -D\beta^3(R - R_e)^3$. Let $R' = (R - R_e)$ and p be the canonical position and momentum operators respectively for the nuclei.

The unperturbed eigenvalues are given by

$$E_n = \omega(n + 1/2). \tag{A.1}$$

The vibrational eigenstates within a given Born-Oppenheimer state are denoted by $|n\rangle$.

Raising and lowering operators are given by [47]

$$A = \sqrt{\frac{\mu\omega}{2}}\,R' + \frac{i}{\sqrt{2\mu\omega}}\,P \quad \text{and} \quad A^\dagger = \sqrt{\frac{\mu\omega}{2}}\,R' - \frac{i}{\sqrt{2\mu\omega}}\,P \tag{A.2}$$

where $\omega = \sqrt{\frac{2D\beta^2}{\mu}}$. These operators acting on the states $|n\rangle$ give

$$A\,|n\rangle = \sqrt{n}\,|n-1\rangle \quad \text{and} \quad A^\dagger\,|n\rangle = \sqrt{n+1}\,|n+1\rangle\,. \tag{A.3}$$

Adding gives

$$A + A^\dagger = \sqrt{2\mu\omega}\,R' \quad \Rightarrow \quad R' = (A + A^\dagger)\sqrt{\frac{1}{2\mu\omega}}. \tag{A.4}$$

Using $H^{(1)} = -D\,\beta^3\,R'^3 \quad \Rightarrow \quad H^{(1)} = -D\,\beta^3\Big(\frac{1}{2\mu\omega}\Big)^{3/2}(\hat{A} + \hat{A}^\dagger)^3$.

Define

$$\gamma \equiv -D\,\beta^3\Big(\frac{1}{2\mu\omega}\Big)^{3/2}. \tag{A.5}$$

We want to find the matrix elements of the perturbation in terms of the unperturbed basis states.

$$\begin{aligned}
H\left|n\right\rangle &= \gamma\,(A+A^{\dagger})(A+A^{\dagger})(A+A^{\dagger})\left|n\right\rangle \\
&= \gamma\,(A+A^{\dagger})(A+A^{\dagger})(\sqrt{n}\left|n-1\right\rangle + \sqrt{n+1}\left|n+1\right\rangle) \\
&= \gamma\,(A+A^{\dagger})(\sqrt{n}\sqrt{n-1}\left|n-2\right\rangle + (n+1)\left|n\right\rangle + n\left|n\right\rangle + \sqrt{n+1}\sqrt{n+2}\left|n+2\right\rangle) \\
&= \gamma\,(A+A^{\dagger})(\sqrt{(n)(n-1)}\left|n-2\right\rangle + (2n+1)\left|n\right\rangle + \sqrt{(n+1)(n+2)}\left|n+2\right\rangle) \\
&= \gamma\,(\sqrt{(n)(n-1)(n-2)}\left|n-3\right\rangle + (2n+1)\sqrt{n}\left|n-1\right\rangle + (n+2)\sqrt{n+1}\left|n+1\right\rangle \\
&\quad + (n-1)\sqrt{n}\left|n-1\right\rangle + (2n+1)\sqrt{n+1}\left|n+1\right\rangle + \sqrt{(n+1)(n+2)(n+3)}\left|n+3\right\rangle) \\
&= \gamma(\sqrt{(n)(n-1)(n-2)}\left|n-3\right\rangle + (3n)\sqrt{n}\left|n-1\right\rangle \\
&\quad + (3n+3)\sqrt{n+1}\left|n+1\right\rangle + \sqrt{(n+1)(n+2)(n+3)}\left|n+3\right\rangle).
\end{aligned} \tag{A.6}$$

To 2^{nd} order the energy of the eigenstates of the Hamiltonian is given by [47]

$$E_n \approx E^{(0)} + \left\langle n\middle|\,\hat{H}^{(1)}\middle|n\right\rangle + \sum_{k\neq n} \frac{\left|\left\langle k\middle|\,\hat{H}^{(1)}\middle|n\right\rangle\right|^2}{E_n^{(0)} - E_k^{(0)}} \tag{A.7}$$

where $E^{(0)}$ is the energy of the unperturbed state and

$$\begin{aligned}
\left\langle k\middle|\,H^{(1)}\middle|n\right\rangle &= \gamma\,(\sqrt{(n)(n-1)(n-2)}\,\delta_{k,n-3} + (3n)\,\sqrt{n}\,\delta_{k,n-1} \\
&\quad + (3n+3)\,\sqrt{n+1}\,\delta_{k,n+1} + \sqrt{(n+1)(n+2)(n+3)}\,\delta_{k,n+3}).
\end{aligned} \tag{A.8}$$

From the Kronecker delta's we see that $\left\langle n\middle|\,\hat{H}^{(1)}\middle|n\right\rangle = 0$. This gives

$$\begin{aligned}
E_n \approx E^{(0)} + \gamma^2\Bigg(&\frac{\left|\sqrt{(n)(n-1)(n-2)}\right|^2}{E_{n+3}^{(0)} - E_n^{(0)}} + \frac{\left|3n\sqrt{n}\right|^2}{E_{n+1}^{(0)} - E_n^{(0)}} \\
&+ \frac{\left|(3n+3)\sqrt{(n+1)}\right|^2}{E_{n-1}^{(0)} - E_n^{(0)}} + \frac{\left|\sqrt{(n+1)(n+2)(n+3)}\right|^2}{E_{n-3}^{(0)} - E_n^{(0)}}\Bigg).
\end{aligned} \tag{A.9}$$

Where

$$\begin{aligned} E^{(0)}_{(n+3)} - E^{(0)}_n &= \omega(n+3+1/2) - \omega(n+1/2) = 3\omega, \\ E^{(0)}_{(n+1)} - E^{(0)}_n &= \omega(n+1+1/2) - \omega(n+1/2) = \omega, \\ E^{(0)}_{(n-1)} - E^{(0)}_n &= \omega(n-1+1/2) - \omega(n+1/2) = -\omega, \\ E^{(0)}_{(n-3)} - E^{(0)}_n &= \omega(n-3+1/2) - \omega(n+1/2) = -3\omega. \end{aligned} \tag{A.10}$$

Inserting (A.1) and (A.10) into (A.9) gives

$$E_n \approx \omega(n+1/2) + \gamma^2\Big(\frac{n(n-1)(n-2)}{3\omega} + \frac{9n^3}{\omega} - \frac{9(n+1)^3}{\omega} - \frac{(n+1)(n+2)(n-+3)}{3\omega}\Big). \tag{A.11}$$

Rearranging the term in brackets gives

$$E_n \approx \omega\Big(n + \frac{1}{2}\Big) - \frac{30\gamma^2}{\omega}\Big(n^2 + n + \frac{11}{30}\Big). \tag{A.12}$$

Using completion of squares on $30(n^2+n)+11$ gives

$$30(n^2+n)+11 = 30\Big(n+\frac{1}{2}\Big)^2 - \frac{30}{4} + 11 = 30(n+1/2)^2 + 7/2. \tag{A.13}$$

Substituting (A.13) into (A.12) gives

$$E_n \approx \omega\Big(n + \frac{1}{2}\Big) - \frac{30\gamma^2}{\omega}\Big(n + \frac{1}{2}\Big)^2 - \frac{7}{2}\frac{\gamma^2}{\omega} \tag{A.14}$$

where from (A.5)

$$\gamma^2 = \frac{D^2\beta^6}{8\mu^3\omega^3} \quad \Rightarrow \quad \frac{\gamma^2}{\omega} = \frac{D^2\beta^6}{8\mu^3\omega^4}. \tag{A.15}$$

Insertion of (A.15) into (A.14) gives

$$E_n \approx \omega\Big(n + \frac{1}{2}\Big) - \frac{15}{4}\frac{D^2\beta^6}{\mu^3\omega^4}\Big(n + \frac{1}{2}\Big)^2 - \frac{7}{16}\frac{D^2\beta^6}{\mu^3\omega^4}. \tag{A.16}$$

From (4.27) we have $\beta^6 = \frac{\omega^6\mu^3}{8D^3}$.

Inserting into (A.16) finally gives

$$E_n \approx \omega\Big(n + \frac{1}{2}\Big) - \frac{{}^2\omega^2}{4D}\Big[\frac{15}{8}\Big(n + \frac{1}{2}\Big)^2 + \frac{7}{32}\Big]. \tag{A.17}$$

Appendix B

SOLUTION OF SCHRÖDINGER EQUATION FOR $J = 0$ AND $\tilde{\epsilon}(R) = D[1 - E^{-\beta(R-R_E)}]^2$

In this appendix we will fill in the details of Morse's solution to the Morse potential [38]. Substitution of the potential $\tilde{\epsilon}(R) = D[1 - e^{-\beta(R-R_e)}]^2$ into the nuclear Schrödinger equation with $J = 0$ gives

$$-\frac{1}{2\mu}\frac{d^2}{dR^2}F(R) + [D - 2\,D\,e^{-\beta(R-R_e)} + D\,e^{-2\beta(R-R_e)}]F(R) - EF(R) = 0. \tag{B.1}$$

Let $\quad y = e^{-\beta(R-R_e)} \quad$ then

$$\frac{dF(R)}{dR} = \frac{dF(y)}{dy}\frac{dy}{dR} = -\beta\,e^{-\beta(R-R_e)}\frac{dF(y)}{dy} = -\beta\,y\frac{dF(y)}{dy} \tag{B.2}$$

and

$$\frac{d^2F(R)}{dR^2} = -\beta\,y\frac{d}{dR}\left(y\frac{dF(y)}{dy}\right) = -\beta\left(\frac{dF(y)}{dy}\frac{dy}{dR} + y\frac{d}{dR}\left(\frac{dF(y)}{dy}\right)\right) \tag{B.3}$$

thus

$$\frac{d^2F(R)}{dR^2} = -\beta\left(-\beta\,y\frac{dF(y)}{dy} - \beta\,y^2\frac{d^2F(y)}{dy^2}\right) = \beta^2y^2\left(\frac{d^2F(y)}{dy^2} + \frac{1}{y}\frac{dF(y)}{dy}\right) \tag{B.4}$$

so that (B.1) becomes

$$\beta^2y^2\left(\frac{d^2F(y)}{dy^2} + \frac{1}{y}\frac{dF(y)}{dy}\right) - 2\mu\big(D - E - 2Dy + Dy^2\big)F(y) = 0. \tag{B.5}$$

Now let

$$F(y) = e^{-z/2}z^{b/2}S(z) \quad \text{where} \quad z = \frac{2}{\beta}\sqrt{2\mu D}\,y \quad \text{and} \quad b = \frac{2}{\beta}\sqrt{2\mu(D-E)} \tag{B.6}$$

so that

$$\begin{aligned}\frac{dF(y)}{dy} = \frac{dS(z)}{dz}\frac{dz}{dy} &= \frac{2}{\beta}\sqrt{2\mu D}\left[-\frac{1}{2}e^{-z/2}z^{b/2}S(z) + \frac{b}{2}e^{-z/2}\frac{z^{b/2}}{z}S(z) + e^{-z/2}z^{b/2}\frac{dS(z)}{dz}\right]\\ &= \frac{2}{\beta}\sqrt{2\mu D}\,e^{-z/2}z^{b/2}\left[\frac{dS(z)}{dz} + \left(\frac{b}{2z} - \frac{1}{2}\right)S(z)\right]\end{aligned} \tag{B.7}$$

and from (B.6), $\quad 1/y = 2/\beta\sqrt{2\mu D}\cdot 1/z \quad$ so that

$$\frac{1}{y}\frac{dF(y)}{dy} = \left(\frac{2}{\beta}\sqrt{2\mu D}\right)^2 e^{-z/2} z^{b/2}\left[\frac{1}{z}\frac{dS(z)}{dz} + \left(\frac{b}{2z^2} - \frac{1}{2z}\right)S(z)\right]. \tag{B.8}$$

Let $\quad \delta = 2/\beta\sqrt{2\mu D} \quad$ so that $\quad z/y = \delta \quad$ and then

$$\frac{1}{y}\frac{dF(y)}{dy} = \delta^2 e^{-z/2} z^{b/2}\left[\frac{1}{z}\frac{dS(z)}{dz} + \left(\frac{b}{2z^2} - \frac{1}{2z}\right)S(z)\right] \tag{B.9}$$

Now using $\quad \frac{d^2F(y)}{dy^2} = \frac{d}{dy}\left(\frac{dS(z)}{dz}\frac{dz}{dy}\right) = \frac{d}{dz}\left(\frac{dS(z)}{dz}\frac{dz}{dy}\right)\frac{dz}{dy} \quad$ we have

$$\begin{aligned}
\frac{d^2F(y)}{dy^2} &= \delta^2 \frac{d}{dz}\left[e^{-z/2} z^{b/2}\left(\frac{dS(z)}{dz} + \left(\frac{b}{2z} - \frac{1}{2}\right)S(z)\right)\right] \\
&= \delta^2\left[-\frac{1}{2}e^{-z/2} z^{b/2}\left(\frac{dS(z)}{dz} + \left(\frac{b}{2z} - \frac{1}{2}\right)S(z)\right) - \frac{b}{2z}e^{-z/2} z^{b/2}\left(\frac{dS(z)}{dz} + \left(\frac{b}{2z} - \frac{1}{2}\right)S(z)\right)\right. \\
&\quad \left. + e^{-z/2} z^{b/2}\left(\frac{d^2S}{dz^2} + \frac{b}{2z}\frac{dS}{dz} - \frac{1}{2}\frac{dS}{dz} - \frac{b}{2z}\frac{dS}{dz}\right)\right] \\
\frac{d^2F(y)}{dy^2} &= \delta^2 e^{-z/2} z^{b/2}\left[\frac{d^2S(z)}{dz^2} + \left(\frac{b}{z} - 1\right)\frac{dS(z)}{dZ} + \left(\frac{b^2}{4z^2} - \frac{b}{2z^2} - \frac{b}{2z} + \frac{1}{4}\right)S(z)\right].
\end{aligned} \tag{B.10}$$

After substituting (B.10) and (B.9) into (B.4) and then (B.4) into (B.1), dividing by $\beta^2\,\delta^2\,y^2\,e^{-z/2}\,z^{b/2}$, and combining like terms we have

$$\frac{d^2S(z)}{dz^2} + \left(\frac{b+1}{z} - 1\right)\frac{dS(z)}{dz} + \left(\frac{b^2}{4z^2} - \frac{(b+1)}{2z} + \frac{1}{4}\right)S(z) - \frac{2\mu}{\beta^2}\frac{y^2}{z^2}\left(\frac{D-E}{y^2} - \frac{2D}{y} + D\right)S(z) = 0 \tag{B.11}$$

where $1/\delta^2 = y^2/z^2$ was used.

The term $D - E$ is equivalent to $-W$ in Morse's paper so that

$$D - E = \frac{b^2\beta^2}{8\mu} \quad \text{but} \quad D = \frac{\beta^2}{8\mu}\frac{z^2}{y^2} \quad \Rightarrow \quad D - E = D\,b^2\,\frac{y^2}{z^2}. \tag{B.12}$$

Substituting D into the third term of (B.11) and rearranging gives

$$-\frac{2\mu}{\beta^2}\frac{y^2}{z^2}\left(\frac{b^2D}{z^2} - \frac{2D}{y} + D\right)S(z) = \left(\frac{-b^2}{4z^2} + \frac{1}{2y} - \frac{1}{4}\right)S(z). \tag{B.13}$$

Substitute (B.13) into (B.11), canceling terms and rearranging gives

$$\frac{d^2S(z)}{dz^2} + \left(\frac{b+1}{z} - 1\right)\frac{dS(z)}{dz} + \frac{1}{z}\left(\frac{\delta}{2} - \frac{(b+1)}{2}\right)S(z) = 0. \tag{B.14}$$

This equation now has the form of the associated Laguerre differential equation [1]

$$\frac{d^2S(z)}{dz^2} + \left(\frac{b+1}{z} - 1\right)\frac{dS(z)}{dz} + \frac{\nu}{z}S(z) = 0. \tag{B.15}$$

The solution will be a finite polynomial if $\frac{\delta}{2} - \frac{(b+1)}{2} = \nu$ where $\nu \in Z$.

Solving for b gives $b = \delta - 1 - 2\nu$, but

$$D - E = \frac{\beta^2\, b^2}{8\mu} = \frac{\beta^2}{8\mu}(\delta - 1 - 2\nu)^2 \quad \text{where} \quad D = \frac{\delta^2\,\beta^2}{8\mu}. \tag{B.16}$$

Solving for E gives

$$E = \frac{\beta^2}{8\mu}(2\delta + 4\delta\nu) - \frac{\beta^2}{8\mu}(4\nu^2 + 4\nu + 1) \quad \text{where} \quad \delta = \frac{2\sqrt{2\mu D}}{\beta}. \tag{B.17}$$

Inserting δ and rearranging gives

$$E = \frac{\beta\sqrt{2\mu D}}{\mu}\left(\nu + \frac{1}{2}\right) - \frac{\beta^2}{2\mu}\left(\nu + \frac{1}{2}\right)^2. \tag{B.18}$$

But $\quad \omega = \sqrt{\frac{2\beta^2 D}{\mu}} \quad$ and $\quad \frac{\beta^2}{\mu} = \frac{\omega^2}{2D}$. Inserting these into (B.18) gives

$$E = \omega\left(\nu + \frac{1}{2}\right) - \frac{\omega^2}{4D}\left(\nu + \frac{1}{2}\right)^2 \tag{B.19}$$

or

$$E = \omega\left[\left(\nu + \frac{1}{2}\right) - \chi\left(\nu + \frac{1}{2}\right)^2\right]. \tag{B.20}$$

where $\quad \chi = \frac{\omega}{4D}$.

Appendix C

SOLUTION OF SCHRÖDINGER EQUATION FOR $J \neq 0$ AND $\tilde{\epsilon}(R) = D[1 - E^{-\beta(R-R_E)}]^2$

Pekeris generalized Morse's solution to the Schrödinger equation by including a non-zero angular momentum contribution. The results of this Appendix were taken from [33, 39]

$$-\frac{1}{2\mu}\frac{d^2}{dR^2}F(R) + \left[\frac{J(J+1)-\Lambda^2}{2\mu R^2} - D[1-e^{-\beta(R-R_e)}]^2\right]F(R) = E\,F(R). \tag{C.1}$$

Rearranging gives

$$\frac{d^2F(R)}{dR^2} + \left[\frac{-J(J+1)+\Lambda^2}{R^2} + 2\,\mu\big(E - D - D\,e^{-2\beta(R-R_e)} + 2\,D\,e^{-\beta(r-r_e)}\big)\right]F(R) = 0. \tag{C.2}$$

As in the case where $J = 0$ let $y = e^{-\beta(R-R_e)}$. This transforms the differential equation into

$$\frac{d^2F(y)}{dy^2} + \frac{1}{y}\frac{dF(y)}{dy} + \frac{2\mu}{\beta^2}\left[\frac{E-D}{y^2} + \frac{2D}{y} - D - \frac{J(J+1)-\Lambda^2}{2\,\mu\,y^2\,R^2}\right]F(y) = 0. \tag{C.3}$$

which we did for the l=0 case. Let $A = \frac{J(J+1)-\Lambda^2}{2\mu R_e}$. Then (C.3) becomes

$$\frac{d^2F(y)}{dy^2} + \frac{1}{y}\frac{dF(y)}{dy} + \frac{2\mu}{\beta^2}\left[\frac{E-D}{y^2} + \frac{2D}{y} - D - \frac{A\,R_e^2}{y^2\,R^2}\right]F(y) = 0. \tag{C.4}$$

Expand R_e^2/R^2 as

$$\frac{R_e^2}{R^2} = \frac{1}{\left(1-\frac{\ln y}{\beta R_e}\right)^2} = 1 + \frac{2}{\beta R_e}(y-1) + \left(-\frac{1}{\beta R_e} + \frac{3}{\beta^2 R_e^2}\right)(y-1)^2 + \ldots \tag{C.5}$$

Inserting this into (C.4) gives

$$\frac{d^2F(y)}{dy^2} + \frac{1}{y}\frac{dF(y)}{dy} + \frac{2\mu}{\beta^2}\left[\frac{E-D-c_0}{y^2} + \frac{2D-c_1}{y} - D - c_0\right]F(y) = 0 \tag{C.6}$$

where

$$c_0 = A\left[1 - \frac{3}{\beta\,R_e} + \frac{3}{\beta^2 R_e^2}\right], \quad c_1 = A\left[\frac{4}{\beta\,R_e} - \frac{6}{\beta^2 R_e^2}\right], \quad c_2 = A\left[-\frac{1}{\beta\,R_e} + \frac{3}{\beta^2 R_e^2}\right]. \tag{C.7}$$

Now making the substitutions

$$\begin{aligned} F(y) &= e^{-z/2} z^{b/2} S(z), \\ z &= 2dy, \\ d^2 &= \frac{2\mu}{\beta^2}(D + c_2), \\ b^2 &= -\frac{8\mu}{\beta^2}(E - D - c_0), \end{aligned}$$

leads to the differential equation

$$\frac{d^2S}{dz^2} + \left(\frac{b+1}{z} - 1\right)\frac{dS}{dz} + \frac{\nu}{z}S = 0$$

where

$$\nu = \frac{2\mu}{\beta^2 d}(2D - c_1) - \frac{1}{2}(b+1).$$

Solving for E gives

$$E_{\nu,J} = D + c_0 - \frac{(D - 1/2\,c_1)^2}{(D + c_2)} + \frac{\beta\hbar(D - 1/2\,c_1)}{\pi\sqrt{2\mu}\sqrt{D + c^2}}\left(\nu + \frac{1}{2}\right) - \frac{\beta^2}{2\mu}\left(\nu + \frac{1}{2}\right)^2. \tag{C.8}$$

Expanding this in terms of c_1/D and c_2/D give

$$\frac{E_{\nu,J}}{c} = \omega\left(\nu + \frac{1}{2}\right) - \chi\omega\left(\nu + \frac{1}{2}\right)^2 + B\big[J(J+1) - \Lambda^2\big] + D\big[J^2(J+1) - \Lambda^2\big]^2 - \alpha(\nu + 1/2)J(J+1) \tag{C.9}$$

where

$$\omega{=}\sqrt{\frac{2\,D\,\beta^2}{\mu}},$$

$$\chi_e = \frac{\omega\,c}{4D},$$

$$B_e = \frac{1}{8\pi\,\mu\,R_e^2\,c},$$

$$D_e = \frac{-1}{16\,\pi^3\,\mu^3\,\omega^2\,c^3\,R_e^6},$$

$$\alpha{=}\frac{3\,\nu}{4\mu\,R^2\,D}\left(\frac{1}{a\,R_e}-\frac{1}{a^2\,R_e^2}\right).$$

As in the $J = 0$ case the first 2 terms represent the vibrational energy of the molecule with correction. The third term is the rotational energy of the molecule treated as a rigid rotor. The fourth term is a centrifugal distortion due to the rotation of the molecule and the fifth terms is rovibrational coupling.

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