

**A High Order Correction of the Energy
of a One Dimensional Model of an H_2^+ Molecule**

Keith Daniel Humfeld

Department of Physics,
Virginia Polytechnic Institute and State University,
Blacksburg, Virginia, 1998.

Thesis submitted to the Faculty of the Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

Master of Science, Physics,
Dr. Schmittman, Dr. Hagedorn, Dr. Williams

Key Words: Born-Oppenheimer Approximation, Δ -doubling, Multiple Scales, Hydrogen.

A High Order Correction of the Energy of a One Dimensional Model of an H_2^+ Molecule

Keith Daniel Humfeld

(ABSTRACT)

The ground state electron wavefunction of some molecules has a non-zero angular momentum about the internuclear axis. Molecular rotational momentum can couple with this angular momentum, splitting the energy degeneracy of the two directions of motion about the internuclear axis. Performing a Born-Oppenheimer approximation of such a system will break the relevant energy degeneracy at eighth order. This degeneracy breaking is known as Λ -doubling.

Topic and Result

The original Born-Oppenheimer approximation dates back to a remarkable paper [1] that appeared only a year after the publication of the Schrodinger equation. That paper contains zeroth order and fourth order expansions for a molecular wave function and energy, respectively. The expansion parameter is ϵ ; the fourth root of the ratio of the electron mass to the nuclear mass. The largest value of ϵ in a realistic model occurs for the hydrogen molecule, where its value is approximately 0.15.

The validity of the result of the expansion was not proven rigorously until 1981 in a paper by Combes, Duclos, and Seiler [2]. In 1987 Hagedorn [3] proved that the expansion could be extended to arbitrarily high powers in epsilon if the potentials between the pairs of particles were assumed to be smooth. In 1988 [4] he generalized this to allow Coulomb potentials in the case of diatomic molecules. In 1992 Klein, Martinez, Seiler, and Wang [5] extended this result to polyatomic molecules and showed that all odd order terms in the expansion for the energy were zero.

The original Born-Oppenheimer approximation provides enormous insight into the structure of molecules. The zeroth order term for the energy is the energy of the electrons and nuclear repulsion with the nuclei fixed at an optimal configuration. The first order correction is zero. The second order term is the harmonic approximation to the energy of vibrations of the nuclei around the optimal configuration. The associated frequencies are derived from the electronic energy near the optimal configuration of the nuclei. The third order term is zero. The fourth order term contains the rotational energy of the whole molecule, the first non-harmonic corrections to the vibrational energy, and a first term that couples the nuclear and electronic motions.

In many situations, the higher order terms have no such simple interpretations; they are merely complicated corrections to the fourth order expansion. However, if the electron state has a non-zero orbital angular momentum about the internuclear axis of a diatomic molecule, then high order terms can introduce splittings of levels that are

degenerate at lower order. If the electrons have an orbital angular momentum of one unit about the internuclear axis, then the splitting occurs at eighth order in the expansion. Many molecules exhibit Λ -doubling when the electrons are in excited states, and a few do so in their ground states.

One molecule in which Λ -doubling occurs in the ground state is Nitric Oxide. An NO molecule has two nuclei and fifteen electrons; the system is intractable. A Hamiltonian for a diatomic molecule is presented by Hagedorn [3]. Instead of considering this Hamiltonian itself, we use a one-dimensional model of an H_2^+ molecule. Note that the one-dimensional model cannot contain Λ -doubling, as that is a three-dimensional effect, and that an H_2^+ molecule does not exhibit Λ -doubling in three dimensions while its electron is in its ground state. However, if the eighth order perturbation of the energy can be found for the one-dimensional model of an H_2^+ molecule, it can be found for an NO molecule through similar calculations.

Although the eighth order correction to the energy of a one dimensional model of an H_2^+ molecule has not been found explicitly, a number of techniques have been developed to aid in the discovery of the correction. These techniques will be mentioned or discussed after the Hamiltonian has been formally derived.

Derivation of Hamiltonian

The model used began as a single electron in a potential described by two “attractive” fixed delta functions:

$$H = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - z\delta(x-a) - z\delta(x+a)$$

The two delta functions were then allowed to move, and were assumed to have a mass of ϵ^{-4} times the mass of the electron. The Hamiltonian was expressed in three coordinates: the positions of each of the three particles. A repulsive term was added to

prevent the two nuclei from approaching each other. In the center of mass frame of reference, it became possible to express the Hamiltonian in two coordinates: the separation (x) of the nuclei and the displacement (y) of the electron from the center of mass of the two nuclei.

$$H = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m} \varepsilon^4 \left[2 \frac{\partial^2}{\partial x^2} + \frac{1}{2} \frac{\partial^2}{\partial y^2} \right] + W(x) - z \delta \left(y - \frac{x}{2} \right) - z \delta \left(y + \frac{x}{2} \right)$$

Another change of variables was enacted, a continuous rescaling, that made the arguments of the delta functions depend only on one variable.

$$H = \frac{\hbar^2}{2m} \left\{ -\varepsilon^4 \frac{\partial^2}{\partial R^2} + \varepsilon^4 \frac{2\alpha}{R} \frac{\partial^2}{\partial R \partial \alpha} - \frac{1}{R^2} \left[(4 + 2\varepsilon^4 + 4\varepsilon^4 \alpha^2) \frac{\partial^2}{\partial \alpha^2} + \varepsilon^4 2\alpha \frac{\partial}{\partial \alpha} \right] \right\} \\ + W(R) - z \frac{2}{R} \delta(\alpha - 1) - z \frac{2}{R} \delta(\alpha + 1)$$

Without this change of variables, the high order expansion formally contains derivatives that do not exist.

The motion of the nuclei had both adiabatic and semi-classical quantum dynamical components, so the R variable corresponding to that motion was broken into two variables. The “multiple-scales technique” was applied to R , resulting in a variable x that corresponded to the classical motion of the nuclei, and a variable y that corresponded to the quantum dynamical motion of the nuclei. Finally, the Hamiltonian used was:

$$H = -\frac{\varepsilon^4}{2} \frac{\partial^2}{\partial x^2} - \varepsilon^3 \frac{\partial^2}{\partial x \partial y} - \frac{\varepsilon^2}{2} \frac{\partial^2}{\partial y^2} + \varepsilon^4 \frac{\alpha}{x} \frac{\partial^2}{\partial x \partial \alpha} + \varepsilon^3 \frac{\alpha}{x} \frac{\partial^2}{\partial y \partial \alpha} \\ - \frac{1}{x^2} \left[(2 + e^4 + 2e^4 a^2) \frac{\partial^2}{\partial \alpha^2} + \varepsilon^4 \alpha \frac{\partial}{\partial \alpha} \right] + \frac{c}{x} - z \frac{2}{x} \delta(\alpha - 1) - z \frac{2}{x} \delta(\alpha + 1) \\ + \sum_{j=4}^{\infty} \varepsilon^j [T_j(x) - T_j(x_0 + \varepsilon y)] + E(x) - E(x_0 + \varepsilon y)$$

Since ϵ is small, $T_j(x_0+\epsilon y)$ and $E(x_0+\epsilon y)$ may be expressed as Taylor expansions about x_0 . This allows the Hamiltonian to be written in a more useful format:

$$\begin{aligned}
H = & \left[\frac{2}{x^2} \frac{\partial^2}{\partial x^2} + \frac{c}{x} - \frac{2z}{x} \delta(\alpha-1) - \frac{2z}{x} \delta(\alpha+1) + E(x_0) - E(x) \right] \\
& + \epsilon^2 \left[-\frac{1}{2} \frac{\partial^2}{\partial y^2} - \frac{E''(x_0)}{2} y^2 \right] - \epsilon^3 \left[\frac{\partial^2}{\partial x \partial y} - \frac{a}{x} \frac{\partial^2}{\partial y \partial \alpha} + \frac{E'''(x_0)}{3!} y^3 \right] \\
& - \epsilon^4 \left[\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{\alpha}{x} \frac{\partial^2}{\partial x \partial \alpha} - \frac{1+\alpha^2}{x^2} \frac{\partial^2}{\partial \alpha^2} - \frac{\alpha}{x^2} \frac{\partial}{\partial \alpha} + \frac{E^{(4)}(x_0)}{4!} y^4 \right] \\
& + \sum_{j=4}^8 \epsilon^j \left[[T_j(x) - T_j(x_0 + \epsilon y)] - \frac{E^{(j)}(x_0)}{j!} y^j \right] + O(\epsilon^9)
\end{aligned}$$

Observations of Variables

At zeroth order in ϵ , Schrodinger's equation is the following:

$$\left[\frac{2}{x^2} \frac{\partial^2}{\partial x^2} + \frac{c}{x} - \frac{2z}{x} \delta(\alpha-1) - \frac{2z}{x} \delta(\alpha+1) + E(x) - E(x_0) - E_0 \right] \Psi_0(x, y, \alpha) = 0$$

E_0 represents the zeroth order approximation of the energy, and $E(x_0)$ is the energy of the unperturbed Hamiltonian. The two are equal, but it is important to not mistake the energy of the Hamiltonian with the approximations of the energy. Schrodinger's equation above can be solved for $X(x, \alpha)$, where $\Psi_0(x, y, \alpha) = Y(y)X(x, \alpha)$. There are an infinite number of solutions, but only the two bound states are of interest. There is an even bound state and an odd bound state, but beneath certain values of z and x , the odd state vanishes. This leads to the idea that in the x and α variables, there are two varieties of states; those mathematically parallel (in α) to the even bound solution and those mathematically perpendicular (in α) to the even bound solution. Only the even bound state is parallel in α to the even bound state; no other state is. This state will be denoted by $\Phi(x, \alpha)$. The even bound state is

$$\Phi(x, \alpha) = \begin{cases} Ae^{k(x)\alpha} & \alpha < -1 \\ B(e^{k(x)\alpha} + e^{-k(x)\alpha}) & -1 < \alpha < 1 \\ Ae^{-k(x)\alpha} & 1 < \alpha \end{cases}$$

but the states perpendicular to $\Phi(x, \alpha)$ vary greatly. In the above expression,

$$B = \frac{Ae^{-k(x)}}{e^{-k(x)} - e^{k(x)}}$$

and A is found by normalization and $k(x)$ satisfies

$$(\tanh(k) + 1) = \frac{xz}{k}$$

The energy of this state is

$$E(x) = -\frac{2k^2(x)}{x^2} + \frac{c}{x}$$

Denoting the states perpendicular to $\Phi(x, \alpha)$ by $F(x, \alpha)$, any wavefunction can be written as

$$Y_1(y)\Phi(x, \alpha) + Y_2(y)F(x, \alpha)$$

At 1st order in ϵ , Schrodinger's equation is similar to zeroth order, but the right side contains a term $E_1\Psi_0(x, y, \alpha)$.

$$[H_{el} - E(x)]\Psi_1(x, y, \alpha) = E_1\Psi_0(x, y, \alpha)$$

The term on the right hand side is parallel to $\Phi(x, \alpha)$, but the Hamiltonian on the left side cancels all functions parallel to $\Phi(x, \alpha)$. The right side of the equation must therefore vanish for all values of x , and α . E_1 is zero and

$$\Psi_1(x, y, \alpha) = \Phi(x, \alpha)Y(y)$$

At 2nd order in ϵ , Schrodinger's equation is

$$[H_{el} - E(x)]\Psi_2(x, y, \alpha) + \left[-\frac{1}{2} \frac{\partial^2}{\partial y^2} - \frac{E''(x_0)}{2} y^2 \right] \Psi_0(x, y, \alpha) = E_2 \Psi_0(x, y, \alpha)$$

This equation can be split into its parallel components and its perpendicular components. $\Psi_2(x, y, \alpha)$ must have no perpendicular component, and is therefore removed from the equation when it is operated on by $[H_{el} - E(x)]$. In the y variable, this is the equation of a simple harmonic oscillator. The well-known solutions to the simple harmonic oscillator are most frequently written in Dirac notation as $|n\rangle$. Any wavefunction will, at some time, be subject to this “simple harmonic oscillator” portion of the Hamiltonian, and can be written as

$$\Psi_m(x, y, \alpha) = \Phi(x, \alpha) \sum_p c_{m,p}(x) |p\rangle + \sum_p F_{m,p}(x, \alpha) |p\rangle$$

where $\Psi_0(x, y, \alpha)$ is

$$\Phi(x, \alpha) |n\rangle$$

It is convenient to use the following substitutions and notation.

$$\begin{aligned} \omega &= \sqrt{E''(x_0)} \\ \rho &= \frac{1}{\sqrt{2\omega}} \\ y &= \rho(a + a^+) \\ \frac{\partial}{\partial y} &= \frac{1}{2\rho}(a - a^+) \end{aligned}$$

The second order correction to the energy is

$$E_2 = \left(n + \frac{1}{2} \right) \omega$$

At 3rd order in ϵ , Schrodinger's equation requires

$$[H_{el} - E(x)]\Psi_3(x, y, \alpha) = \left[\frac{1}{2\rho} \left(\frac{\partial}{\partial x} - \frac{\alpha}{x} \frac{\partial}{\partial \alpha} \right) (a - a^+) \Psi_0 \right]^\perp$$

to be solved for $\Psi_3(x,y,\alpha)$, where the right hand side of the equation is the component of that expression that is perpendicular in α to $\Phi(x,\alpha)$. By earlier considerations, $\Psi_3(x,y,\alpha)$ can be written as

$$\Phi(x,\alpha) \sum_p c_{3,p}(x) |p\rangle + F_{3,n-1}(x,\alpha) |n-1\rangle + F_{3,n+1}(x,\alpha) |n+1\rangle$$

where $F_{3,n\pm 1}(x,\alpha)$ are found by the constraining equation.

At 4th order, Schrodinger's equation has similar requirements for $F_{4,n\pm 4}(x,\alpha)$ and $F_{4,n\pm 2}(x,\alpha)$. These will be the same as $F_{3,n\pm 1}(x,\alpha)$, multiplied by certain expressions. The equation for $F_{4,n}(x,\alpha)$ is sufficiently more difficult, but still solvable.

$$\begin{aligned} [H_{el} - E(x)]\Psi_4(x,y,\alpha) = & \left[\frac{1}{2\rho} \left(\frac{\partial}{\partial x} - \frac{\alpha}{x} \frac{\partial}{\partial \alpha} \right) (a - a^+) \Psi_1(x,y,\alpha) \right]^\perp \\ & + \left[\left(\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{\alpha}{x} \frac{\partial^2}{\partial x \partial \alpha} - \frac{1 + \alpha^2}{x^2} \frac{\partial^2}{\partial \alpha^2} - \frac{\alpha}{x^2} \frac{\partial}{\partial \alpha} \right) \Psi_0(x,y,\alpha) \right]^\perp \end{aligned}$$

Discovering Necessary Terms

Now that the structure of the solutions has been found, it is possible to calculate each of the components of each of the wavefunctions until E_8 is found. Many terms, however, do not contribute to E_8 . By examining which terms contribute to E_8 , and which terms contribute to those terms, it is possible to discover which terms are necessary, and which do not need to be calculated.

Finding Terms

Knowing the structure and necessary terms, it is possible to compute the terms in an efficient manner. Note that each term $c_{m,p}(x)$ (the x -dependent coefficient of each $|p\rangle$) will be a function of the terms that have been previously calculated. The coefficients $c_{1,p}(x)$ can be found by examination of Schrodinger's equation in third order of ϵ .

$$\begin{aligned} [H_{el} - E(x)]\Psi_3(x,y,\alpha) + [H_{osc} - E_2]\Psi_1(x,y,\alpha) = \\ \left[\frac{1}{2\rho} (a - a^+) \left(\frac{\partial}{\partial x} - \frac{\alpha}{x} \frac{\partial}{\partial \alpha} \right) + \frac{E'''(x_0)}{3!} (a + a^+)^3 - E_3 \right] \Psi_0(x,y,\alpha) \end{aligned}$$

The projection of this equation onto the “parallel to $\Phi(x,\alpha)$ ” direction is

$$[H_{osc} - E_2] \Phi(x, \alpha) \sum_p c_{1,p}(x) |p\rangle = \left[\frac{1}{2\rho} (a - a^+) \left(\frac{\partial}{\partial x} - \frac{\alpha}{x} \frac{\partial}{\partial \alpha} \right) + \frac{E'''(x_0)}{3!} \rho^3 (a + a^+)^3 \right] \Phi(x, \alpha) |n\rangle$$

The four nonzero coefficients $c_{1,p}(x)$ are

$$\begin{aligned} c_{1,n-3}(x) &= -\frac{1}{3} \frac{E'''(x_0)}{3!} \rho^3 (\sqrt{n-2} \sqrt{n-1} \sqrt{n}) \\ c_{1,n-1}(x) &= -\frac{1}{1} \frac{E'''(x_0)}{3!} \rho^3 ((3)(n)\sqrt{n}) - \frac{1}{2\rho} \left[\left(\frac{\partial}{\partial x} - \frac{\alpha}{x} \frac{\partial}{\partial \alpha} \right) \Phi(x, \alpha) \right] (\sqrt{n}) \\ c_{1,n+1}(x) &= \frac{1}{1} \frac{E'''(x_0)}{3!} \rho^3 ((3)(n+1)\sqrt{n+1}) - \frac{1}{2\rho} \left[\left(\frac{\partial}{\partial x} - \frac{\alpha}{x} \frac{\partial}{\partial \alpha} \right) \Phi(x, \alpha) \right] (\sqrt{n+1}) \\ c_{1,n+3}(x) &= \frac{1}{3} \frac{E'''(x_0)}{3!} \rho^3 (\sqrt{n+3} \sqrt{n+2} \sqrt{n+1}) \end{aligned}$$

where the parallel bars imply the projection of the function inside the brackets onto $\Phi(x,\alpha)$, or the mathematical dot-product of the interior function with $\Phi(x,\alpha)$, in the α variable.

A careful reader may note that the equation above puts no restriction on $c_{1,n}(x)$. We will choose $c_{1,n}(x) = 0$. By doing so, we have decided that $\Psi_1(x,y,\alpha)$ is orthogonal to $\Psi_0(x,y,\alpha)$, in particular, it is mathematically perpendicular to $\Psi_0(x,y,\alpha)$ in the y variable. Making this choice will only affect the normalization of $\Psi_0(x,y,\alpha)$. We will choose a similar restriction on all corrections to the wavefunctions:

$$c_{m,n}(x) = 0$$

At fourth order in ε , the parallel component of Schrodinger's equation is

$$\begin{aligned} \sum_p (p-n)c_{2,p}(x)|p\rangle &= \left[\frac{1}{2\rho}(a-a^+) \left(\frac{\partial}{\partial x} - \frac{\alpha}{x} \frac{\partial}{\partial \alpha} \right) + \frac{E'''(x_0)}{3!}(a+a^+)^3 \right] \sum_q c_{1,q}(x)|q\rangle \\ &+ \left[\left(\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{\alpha}{x} \frac{\partial^2}{\partial x \partial \alpha} - \frac{1+\alpha^2}{x^2} \frac{\partial^2}{\partial \alpha^2} - \frac{\alpha}{x^2} \frac{\partial}{\partial \alpha} \right) \Phi(x, \alpha) \right] |n\rangle \\ &+ \left[\frac{E^{(4)}}{4!} \rho^4 (a+a^+)^4 - T_4(x) + T_4(x_0) + E_4 \right] |n\rangle \end{aligned}$$

There are six nonzero $c_{2,p}(x)$:

$$c_{2,n-6}(x) = -\frac{1}{6} \frac{E'''(x_0)}{3!} \rho^3 (\sqrt{n-5}\sqrt{n-4}\sqrt{n-3}c_{1,n-3})$$

$$\begin{aligned} c_{2,n-4}(x) &= -\frac{1}{4} \frac{E'''(x_0)}{3!} \rho^3 (\sqrt{n-3}\sqrt{n-2}\sqrt{n-1}c_{1,n-1} + \sqrt{n-3}(3)(n-3)c_{1,n-3}) \\ &- \frac{1}{4} \frac{E^{(4)}(x_0)}{4!} \rho^4 \sqrt{n-3}\sqrt{n-2}\sqrt{n-1}\sqrt{n} - \frac{1}{4} \frac{1}{2\rho} (D_1 \Phi^{\parallel}) (\sqrt{n-3}c_{1,n-3}) \end{aligned}$$

$$\begin{aligned} c_{2,n-2}(x) &= -\frac{1}{2} \frac{E'''(x_0)}{3!} \rho^3 (\sqrt{n-2}(3)(n-2)c_{1,n-3} + \sqrt{n-1}(3)(n-1)c_{1,n-1} + \sqrt{n-1}\sqrt{n}\sqrt{n+1}c_{1,n+1}) \\ &- \frac{1}{2} \frac{E^{(4)}(x_0)}{4!} \rho^4 \sqrt{n-1}\sqrt{n}(4n-2) - \frac{1}{2} \frac{1}{2\rho} (D_1 \Phi^{\parallel}) (\sqrt{n-1}c_{1,n-1} - \sqrt{n-2}c_{1,n-3}) \\ &- \frac{1}{2} \frac{1}{2\rho} \sqrt{n-1}c'_{1,n-1} \end{aligned}$$

$$\begin{aligned} c_{2,n+2}(x) &= \frac{1}{2} \frac{E'''(x_0)}{3!} \rho^3 (\sqrt{n+2}\sqrt{n+1}\sqrt{n}c_{1,n-1} + \sqrt{n+2}(3)(n+2)c_{1,n+1} + \sqrt{n+3}(3)(n+3)c_{1,n+3}) \\ &+ \frac{1}{2} \frac{E^{(4)}(x_0)}{4!} \rho^4 \sqrt{n+2}\sqrt{n+1}(4n+6) + \frac{1}{2} \frac{1}{2\rho} (D_1 \Phi^{\parallel}) (\sqrt{n+3}c_{1,n+3} - \sqrt{n+2}c_{1,n+1}) \\ &- \frac{1}{2} \frac{1}{2\rho} \sqrt{n+2}c'_{1,n+1} \end{aligned}$$

$$\begin{aligned} c_{2,n+4}(x) &= \frac{1}{4} \frac{E'''(x_0)}{3!} \rho^3 (\sqrt{n+4}\sqrt{n+3}\sqrt{n+2}c_{1,n+1} + \sqrt{n+4}(3)(n+4)c_{1,n+3}) \\ &+ \frac{1}{4} \frac{E^{(4)}(x_0)}{4!} \rho^4 \sqrt{n+4}\sqrt{n+3}\sqrt{n+2}\sqrt{n+1} - \frac{1}{4} \frac{1}{2\rho} (D_1 \Phi^{\parallel}) (\sqrt{n+4}c_{1,n+3}) \end{aligned}$$

$$c_{2,n+6}(x) = \frac{1}{6} \frac{E'''(x_0)}{3!} \rho^3 \sqrt{n+6}\sqrt{n+5}\sqrt{n+4}c_{1,n+3}$$

$$(D_1\Phi^\parallel) = \left[\left(\frac{\partial}{\partial x} - \frac{\alpha}{x} \frac{\partial}{\partial \alpha} \right) \Phi(x, \alpha) \right]^\parallel$$

It is illustrated that the coefficients $c_{m,p}(x)$ are functions on the previous coefficients $c_{m-1,p}(x)$. Performing the expansion without substituting in the $c_{m-1,p}(x)$ will allow for simple correction of sign mistakes and any algebraic errors.

All necessary coefficients $c_{m,p}(x)$ may be found in a manner similar to the above, but will not be included in this paper due to their collective lengths.

At fourth order in ε , Schrodinger's equation allows $T_4(x)$ to be found.

$$\begin{aligned} T_4(x) = & \frac{E'''(x_0)}{3!} \rho^3 \left(\sqrt{n-2}\sqrt{n-1}\sqrt{n}c_{1,n-3} + \sqrt{n}(3)(n)c_{1,n-1} + \sqrt{n+1}(3)(n+1)c_{1,n+1} \right. \\ & \left. + \sqrt{n+3}\sqrt{n+2}\sqrt{n+1}c_{1,n+3} \right) \\ & + \frac{E^{(4)}(x_0)}{4!} \rho^4 (3)(2n^2 + 2n + 1) + (D_2\Phi^\parallel) + \frac{1}{2\rho} \left(\sqrt{n+1} \frac{\partial c_{1,n+1}}{\partial x} - \sqrt{n} \frac{\partial c_{1,n-1}}{\partial x} \right) \\ (D_2\Phi^\parallel) = & \left[\left(\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{\alpha}{x} \frac{\partial^2}{\partial x \partial \alpha} - \frac{1+\alpha^2}{x^2} \frac{\partial^2}{\partial \alpha^2} - \frac{\alpha}{x^2} \frac{\partial}{\partial \alpha} \right) \Phi(x, \alpha) \right]^\parallel \end{aligned}$$

With $T_4(x)$ written in this manner, $E_4 = T_4(x_0)$.

$$\begin{aligned} E_4 = & \frac{1}{E''(x_0)} \left[\left(\frac{E'''(x_0)}{E''(x_0)} \right)^2 \left(\frac{11}{288} + \frac{5n(n+1)}{48} \right) + \left(\frac{E^{(4)}(x_0)}{E''(x_0)} \right) \left(\frac{1}{32} + \frac{n(n+1)}{16} \right) \right] \\ & + (D_2\Phi^\parallel) + \frac{1}{2\rho} \left(\sqrt{n+1} \frac{\partial c_{1,n+1}}{\partial x} - \sqrt{n} \frac{\partial c_{1,n-1}}{\partial x} \right) \end{aligned}$$

This is the Born-Oppenheimer prediction of the fourth order correction of the energy, with a pair of additional terms attributed to the specific model under consideration.

The sixth order and eighth order corrections to the energy can be found in a like manner, however the additional terms are exceedingly more complex and some components of those terms have not been evaluated. There are mathematical difficulties

associated with calculating the perpendicular components $F_{m,p}(x)$, and worse, the parallel and perpendicular components of D_1 and D_2 acting on these functions.

In Conclusion

There are mathematical difficulties in finding the eighth order correction to the energy of the examined model. One may bypass these difficulties by leaving undetermined terms in each expression, or by choosing convenient notation that allows these math problems to be solved separately. After so doing, the eighth order correction to the energy is possible to find, although finding it is extremely tedious. Noting that only some terms of the corrections of the wavefunctions contribute to E_8 allows a solution to be found more quickly. Making observations of the behavior of the wavefunction in its three variables allows clever notation to be used, thus reducing the difficulty of finding E_8 . Noting that any correction of the wavefunction depends explicitly on the prior corrections of the wavefunction, a solution may be found modularly, or even step-by-step backwards from E_8 . Writing each wavefunction as an explicit function of the prior wavefunctions will stop sign errors and small algebraic errors from propagating into higher order corrections.

Proper use of these techniques will save much time when solving for the eighth order correction of the energy of an electron in an NO molecule, that is, when attempting to observe Λ -doubling theoretically.

References

1. Born, M., Oppenheimer, R. Zur Quantentheorie der Molekeln. Ann. Phys. (Leipzig) 84, 457-484 (1927).
2. Combes, J.-M., Duclos, P., Seiler, R. The Born-Oppenheimer Approximation. in Rigorous Atomic and Molecular Physics, ed by Velo, G., Wightman, A. pp. 185-212. New York: Plenum Press 1981.
3. Hagedorn, G. High Order Corrections to the Time-Independent Born-Oppenheimer Approximation. I: Smooth Potentials. Ann. Inst. H. Poincare Sect A. 47, 1-19 (1987).
4. Hagedorn, G. High Order Corrections to the Time-Independent Born-Oppenheimer Approximation. II: Diatomic Coulomb Systems. Commun. Math. Phys. 116, 23-44 (1988).
5. Klein, M., Martinez, A., Seiler, R., Wang, X. P. On the Born-Oppenheimer Expansion for Polyatomic Molecules. Commun. Math. Phys. 143, 607-639 (1992).

Keith Daniel Humfeld

Permanent Address:

2310 Archdale Rd
Reston, Va. 20191

Education: Virginia Polytechnic Institute and State University; Blacksburg, VA

M.S. Physics, Expected August 1998

B.S. Physics, May 1997

B.S. Mathematics, May 1997