

ASYMPTOMIC SOLUTIONS OF THE BORN-OPPENHEIMER NUCLEAR EQUATION WITH THE FROST-MUSULIN POTENTIAL FUNCTION

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ABSTRACT. — The asymptotic solutions of the Born-Oppenheimer equation for a particular semi-empirical potential are discussed. Some mathematical equations and functions are used, for the first time, in a chemical problem. A formal demonstration is given of the common notion that a molecule is a perturbed atom.

In the Born-Oppenheimer approximation, (Slater, 1963) the equation for the nuclear motion of a diatomic molecule is

$$\left[-\frac{1}{2M_1} \nabla_1^2 - \frac{1}{2M_2} \nabla_2^2 + E(X_1, Y_1, Z_1, X_2, Y_2, Z_2) \right] v((X_1, Y_1, Z_1, X_2, Y_2, Z_2)) = \mathcal{E} v(X_1, Y_1, Z_1, X_2, Y_2, Z_2) \quad (1)$$

where the M_i are the masses of the nuclei, ∇_i^2 are the Laplacian operators representing the kinetic energy operators of the nuclei, $E(X_i, Y_i, Z_i)$ is the energy solution of the Schrödinger equation for fixed nuclei which serves as the potential energy function in Equation (1), $v(X_i, Y_i, Z_i)$ is the wave function, and $\mathcal{E}$ is the approximate eigenvalue to the exact Schrödinger equation. Equation (1) is stated in atomic units. (Energy: 1 hartree = 27.210 eV; Mass: 1 a.u. = 9.1083 x 10⁻²⁸g; Length: 1 bohr

= 0.52917 x 10⁻⁸ cm; Charge: 1 a.u. = 4.80286 x 10⁻¹⁰ e.s.u.)

After the usual change of coordinates, the separation of angular wave functions, and the introduction of the radial probability function, $P(r)$, where

$$P(r) = rR(r) \quad (2)$$

the following differential equation for the function $P(r)$ is obtained.

$$\frac{d^2P}{dr^2} + 2\mu \left[\mathcal{E} - E(r) - \frac{\Lambda}{2\mu r^2} \right] P = 0 \quad (3)$$

where $R(r)$ is the radial portion of $v(X_i, Y_i, Z_i)$, $E(r)$ is that portion of the potential energy function which is independent of angles, Λ is a separation constant, and μ is the reduced mass (Eyring, et al., 1944). If the constant Λ is set to zero, the equation for the lowest rotational state is obtained.

$$\frac{d^2P}{dr^2} + 2\mu [\mathcal{E} - E(r)] P = 0 \quad (4)$$

One may reintroduce the rotational problem by considering the term containing Λ as a perturbation to Equation (4). The purpose of this note is to investigate the solutions to Equation (4) if $E(r)$ is given by the semiempirical potential energy function suggested by Frost and Musulin (1954). Substitution

of their $E(r)$ into Equation (4) yields

$$\frac{d^2P}{dr^2} + 2\mu \left[\epsilon - e^{-ar} \left(\frac{1}{r} - b \right) \right] P = 0 \quad (5)$$

where a and b are constants, order of magnitude of 1 and minimum order of magnitude of 1, respectively.

LARGE r

For very large values of the internuclear distance, the potential energy terms of Equation (4) vanish. The asymptotic solutions correspond to those of a free wave ($\epsilon > 0$) or an exponential function ($\epsilon < 0$).

For molecules with moderately large values of b , at least $0(10^2)$, and with values of the internuclear distance such that $1/r$ becomes negligible compared to b , Equation (5) becomes

$$\frac{d^2P}{dr^2} + 2\mu \left[\epsilon + be^{-ar} \right] P = 0 \quad (6)$$

The substitutions

$$\gamma^2 = \frac{-8\mu\epsilon}{a^2} \quad z = \frac{2(2\mu b)^{1/2}}{a} e^{-ar/2}$$

transform Equation (6) into

$$z^2 \frac{d^2P}{dz^2} + z \frac{dP}{dz} + (z^2 - \gamma^2) P = 0 \quad (7)$$

which is the standard form of the differential equation whose general solution for $\epsilon < 0$ is

$$P = c_1 J_\gamma(z) + c_2 Y_\gamma(z) \quad (8)$$

where $J_\gamma(z)$ and $Y_\gamma(z)$ are Bessel functions of the first kind and of the

second kind, respectively, and c_1 and c_2 are arbitrary constants (Abramowitz and Stegun, 1964). The constant c_2 must be taken as zero since $Y_\gamma(z)$ is unbounded as z approaches zero, i.e., as r approaches infinity.

For $\epsilon > 0$, the asymptotic solutions are Bessel functions of imaginary order whose series solutions are known (Watson, 1944). Mathematically, the results are consistent with the results which one obtains at infinite internuclear distances where the potential function vanishes.

SMALL r

For small values of the internuclear distance, the exponential of the potential function may be expanded about zero; whence, retaining terms through order of r^0 , one obtains

$$\frac{d^2P}{dr^2} + \left\{ 2\mu \left[\epsilon - \frac{1}{r} + (a+b) \right] \right\} P = 0 \quad (9)$$

If one lets

$$2\mu [\epsilon + (a+b)] = -s^2$$

Equation (8) becomes

$$\frac{d^2P}{dr^2} - \left[s^2 + \frac{2\mu}{r} \right] P = 0 \quad (10)$$

which is an example of the Hamburger equation of the second order (Ince, 1944).

The necessary condition that Equation (10) have a normal solution is

$$\epsilon = -\frac{\mu}{2n^2} - (a+b) \quad (11)$$

where n is a positive integer. Alternatively, the same condition can be obtained by requiring proper be-

havior of the solution found by the method of undetermined coefficients. That is, Equation (11) is the condition for obtaining a set of polynomials as solutions to Equation (9).

The probability function obtained from Equation (10) is a Bateman function (Bateman, 1931). Like the Bessel function it is a special case of a confluent hypergeometric function.

The condition given in Equation (11) provides an interesting physical picture of molecular formation. The quantity $-(a + b)$ is the "united"

atom energy, V_e^0 , whereas the first term in Equation (11) is simply the energy of a hydrogen-like atom. Thus, for very small internuclear distances, a diatomic molecule behaves like an atom with a zero of energy equal to V_e^0 . This physical

behavior provides verification of the intuitive concept that a molecule, at small distances, is a perturbed atom.

Since V_e^0 corresponds to the leading term of the expansion given by Brown and Steiner (1966), Equation (11) generalizes the information concerning the molecular electronic energy near the united atom to information concerning the total molecular energy near the united atom.

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