

Some One Dimensional Atomic Potential Functions

JOHN A. RICKETTS and LARRY D. NICHOLS, DePauw University

The problem of finding a one dimensional potential field which gives a one dimensional wave function exactly analogous to that found through the solution of the appropriate three dimensional Schrodinger equation might offer a useful approach to chemical bonding approximations. In the following treatment such functions will be developed for any s or p state of a hydrogen-like atom or ion.

The ground state wave function for the hydrogen atom is

$$\Psi = \exp (-r) \quad (1)$$

where r represents the radial distance from the nucleus as measured in atomic units (1). The normalizing constant has been omitted from eq. 1 since its inclusion is unnecessary for the present discussion. The one dimensional analogue of eq. 1 is

$$\Psi = \exp (-|x|). \quad (2)$$

Equation 2 must satisfy the one dimensional Schrodinger equation which when expressed in atomic units is

$$-\frac{1}{2} \frac{d^2 \Psi}{dx^2} + V \Psi = E \quad (3)$$

for some potential function V . The potential function may be written as the sum of two contributions, $V = V_o + V_x$. V_o is its form at the nucleus, $x = 0$, and V_x is its form for $x \neq 0$. In addition the potential function must be such that as $|x| \rightarrow \infty$, $V \rightarrow 0$, and must not be zero everywhere.

The dimensionless electronic energy associated with 1s state for the hydrogen atom is $E = -\frac{1}{2}$; therefore, the potential function must vanish at all points other than at the nucleus. To determine its nature at the nucleus multiply eq. 3 by dx and integrate the expression,

$$-\frac{1}{2} \int_{-\epsilon}^{+\epsilon} \frac{d^2 \Psi}{dx^2} dx + \int_{-\epsilon}^{+\epsilon} V \Psi dx = \int_{-\epsilon}^{+\epsilon} E \Psi dx \quad (4)$$

between the limits $-\epsilon$ and $+\epsilon$ where ϵ is an infinitesimal interval of length on either side of the nucleus. Let ϵ approach zero. Since Ψ is well-

behaved, it is finite at the nucleus; therefore, $\lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{+\epsilon} \Psi dx$ vanishes. The

quantity, $\int_{-\epsilon}^{+\epsilon} \frac{d^2 \Psi}{dx^2} dx$, becomes $\Delta \left[\frac{d \Psi}{dx} \right]_{x=0}$, the change in the slope of the wave function in passing through the origin in a positive direction. For the wave function, $\exp (-|x|)$, $\Delta \left[\frac{d \Psi}{dx} \right]_{x=0} = -2$. Consequently, it is

necessary that

$$\lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{+\epsilon} V \psi \, dx = \psi(0) \lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{+\epsilon} V \, dx = -1 \quad (5)$$

The conditions that a function, $f(x)$, be zero for $x \neq 0$ and that

$$\int_{-\infty}^{+\infty} f(x) \, dx = -1 \text{ defines a negative Dirac delta function (2) of unit}$$

strength placed at the origin. For the one dimensional 1s state for the hydrogen atom, $V = -\delta(x)$. Table 1 summarizes those potential func-

TABLE 1

One Dimensional Potential Functions for the Hydrogen Atom

Energy States	Wave Function	Potential Function
1s	$\exp(- x)$	$-\delta(x)$
2s	$(2 - x) \exp(-\frac{ x }{2})$	$\frac{1}{2} \frac{1}{(2 - x)} - \delta(x)$
2p	$x \exp(-\frac{ x }{2})$	$-\frac{1}{2 x }$
3s	$(27 - 18 x + 2 x ^2) \exp(-\frac{ x }{3})$	$\frac{4}{81} \frac{(6 - x)}{54 x + 6x^2} - \delta(x)$
3p	$(6 - x) x \exp(-\frac{ x }{3})$	$\frac{2 x }{18 x - 3x^2} - \frac{7}{3x^2}$

tions that yield the correct one dimensional 1s, 2s, 2p, 3s, and 3p wave functions for the hydrogen atom. It is interesting to note that each of these potentials may be described as the sum of a set of rectangular hyperbolas, each member of which has its vertical asymptote at a node of the corresponding wave function.

Frost (3), (4), (5) has employed the Dirac delta function model to treat one electron atoms, diatomic molecules, and aromatic systems. The advantage of his model is that the linear combination of atomic orbitals is an exact solution of the Schrodinger equation. With this model correct united atom and separated atom electronic energies are realized for H_2^+ ; in the case of aromatic nuclei it predicts excitation energies, resonance energies, and ionization potentials for the pi electrons. The disadvantage of the model is inherent in the fact that inter-electronic interactions are not treated, and in the case of diatomic molecules the nuclear repulsion term must be modified in order to obtain the desired minimum in the potential energy curve. It should be stated here that Frost (6) conceived the delta function model through coulombic considerations and not in the manner presented in this paper.

In this next section the general problem of an electron moving in a field that is described by three delta functions will be discussed. The potential function is of the form

$$V = g \delta \left(x + \frac{R}{2} \right) + g_0 \delta (x) + g \delta \left(x - \frac{R}{2} \right) \quad (6)$$

where g and g_0 are the delta function strengths which may be positive or negative and $\frac{R}{2}$ in atomic units represents the displacement of the

delta function from the origin. The appropriate wave function can be represented as a linear combination of atomic orbitals having the form

$$\Psi = A \exp \left(-c \left| x + \frac{R}{2} \right| \right) + B \exp (-c |x|) + C \exp \left(-c \left| x - \frac{R}{2} \right| \right) \quad (7)$$

except at the points, $+\frac{R}{2}$ and zero. The energy is given as $E = -\frac{c^2}{2}$.

In order to solve the wave equation it is necessary to apply the delta function condition at each delta function. This condition is outlined below for the point $+\frac{R}{2}$.

$$-\frac{1}{2} \left[\frac{d^2 \Psi}{dx^2} \right]_{R/2-}^{R/2+} + \int_{R/2-}^{R/2+} g \delta \left(x - \frac{R}{2} \right) \Psi dx = \int_{R/2-}^{R/2+} E \Psi dx \quad (8)$$

$$-\frac{1}{2} \Delta \left[\frac{d \Psi}{dx} \right]_{R/2} + g \Psi \left(\frac{R}{2} \right) = 0 \quad (9)$$

Application of the above condition at each of the three points leads to the following secular equation for a non-trivial solution,

$$\begin{vmatrix} g + c & g \exp \left(-\frac{cR}{2} \right) & g \exp (-cR) \\ g_0 \exp \left(-\frac{cR}{2} \right) & g_0 + c & g_0 \exp \left(-\frac{cR}{2} \right) \\ g \exp (-cR) & g \exp \left(-\frac{cR}{2} \right) & g + c \end{vmatrix} = 0 \quad (10)$$

Equation 10 reduces to the equality that

$$\exp (-cR) = \frac{(g + c)(g + c)}{g(g_0 - c)} \quad (11)$$

with the values for the normalizing constants expressed in terms of A given as

$$C = A$$

$$B = -A \left[\left(1 + \frac{c}{g} \right) \exp \left(+\frac{cR}{2} \right) + \exp \left(-\frac{cR}{2} \right) \right] \quad (12)$$

If the negative sign in eq. 11 is adopted, the solution reduces to the nodal (higher energy) solution of the symmetrical two delta function model discussed by Frost (reference 4). When the positive sign is assumed, non-nodal possibilities result, the forms of which depend upon the relative

magnitudes of the delta function strengths, g and g_0 , and the value of the parameter c . The permitted values of g, g_0 , and c can be determined through the analysis of the inequality,

$$0 < \frac{(g + c)(g_0 + c)}{g(g_0 - c)} < 1$$

The results of this analysis are summarized in Figure 1 which was constructed using the fact that for a non-nodal solution the ratio

$$\frac{\Psi(O)}{\Psi(R)} = - \frac{2g}{g_0 + c} \left\{ \frac{(g + c)(g_0 + c)}{g(g_0 - c)} \right\}^{\frac{1}{2}} \quad (14)$$

must be greater than zero; therefore $\frac{g}{g_0 + c}$ must be negative. In the

figure the delta function strength g_0 is plotted as abscissa in units of the parameter c while the delta function strength g is plotted as ordinate in the same units. Within the allowed areas are sketched the forms of the wave functions.

Literature Cited

1. W. KAUFMANN, "Quantum Chemistry," Academic Press Inc., New York, (1957), p. 176.
2. L. I. SCHIFF, "Quantum Mechanics," McGraw-Hill Book Company Inc., New York, (1949), p. 50.
3. A. A. FROST, J. Chem. Phys., **22**, 1613 (1954).
4. A. A. FROST, J. Chem. Phys., **23**, 1150 (1956).
5. A. A. FROST and F. E. LELAND, J. Chem. Phys., **25**, 1154 (1956).
6. A. A. FROST, private communication.

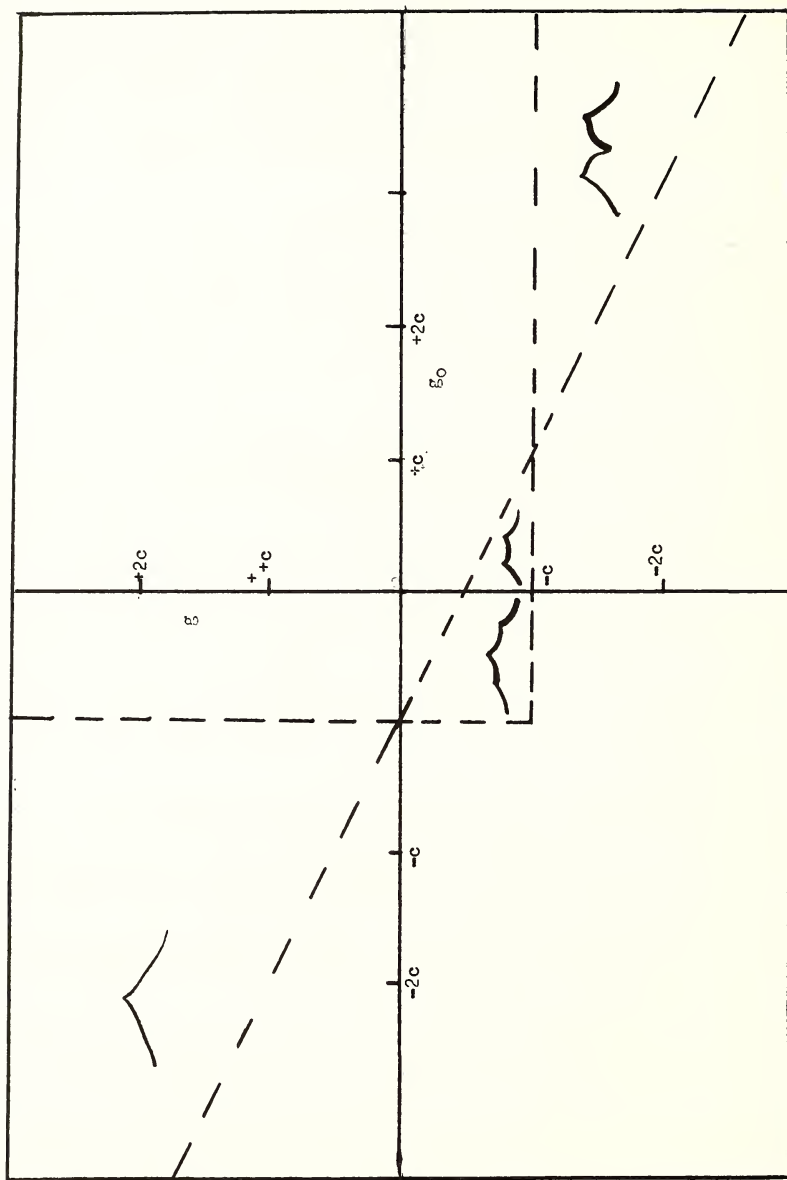


Figure 1. Regions of Existence of Non-nodal Wave Functions for the Three Delta Function Model.