

# Visualizing Valence Bond Eigenfunctions

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(Dated: June 28, 2004)

## ABSTRACT

Schemes for drawing and visualizing valence bond wavefunctions are presented and discussed.

*Note. This manuscript will be converted to Word if accepted for publication.*

## I. INTRODUCTION

Although great efforts (1) have been made to encourage students to visualize atomic orbitals (2,3), less efforts have been expended in teaching students how to visualize valence bond wavefunctions. Perhaps, this accounts for the lack of interest in teaching this alternative model (to molecular orbital theory) in standard physical chemistry courses. Certainly, the discussion of Hoffmann et al (4) indicates a continuing unhappiness with the state of understanding and enjoyment of valence bond theory.

In this contribution, the schemes employed for visualizing molecular orbitals are extended to include valence bond orbitals.

## II. THE GROUND STATE OF THE $H_2$ MOLECULE

We take it as a given that (in atomic units) the valence bond wave function for the ground state of hydrogen is given by the following equivalent statements:

$$\psi_{VB} = [1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

which, for the spatial part of the wave function, we translate into

$$\psi_{VB} = [e^{-r_A(1)}e^{-r_B(2)}] + [e^{-r_A(2)}e^{-r_B(1)}]$$

which we translate one more time into Cartesian Coördinates (see Figure 1) thusly

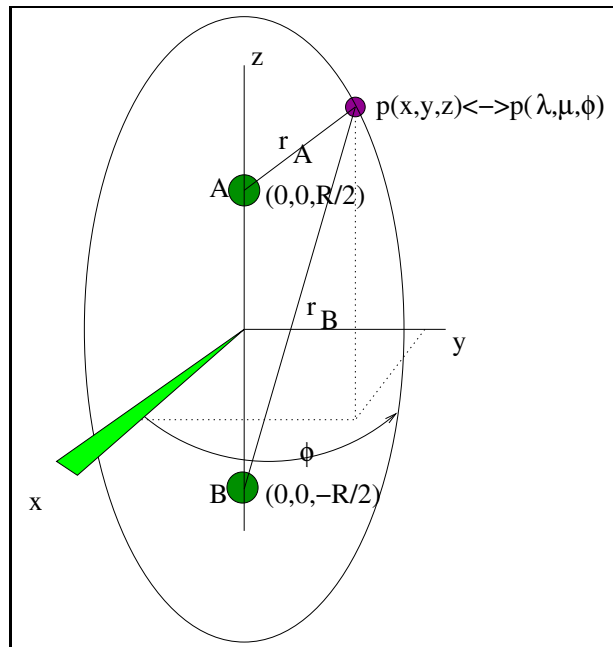


FIG. 1: The Standard Coördinate Scheme for  $H_2^+$  and other two-center problems.

$$\psi_{VB}(x_1, y_1, z_1, x_2, y_2, z_2) = e^{-\sqrt{x_1^2+y_1^2+(z_1-R/2)^2}} e^{-\sqrt{x_2^2+y_2^2+(z_2+R/2)^2}} + e^{-\sqrt{x_2^2+y_2^2+(z_2-R/2)^2}} e^{-\sqrt{x_1^2+y_1^2+(z_1+R/2)^2}}$$

where, of course, the bond length is “R”.

Contrary to molecular orbital theory, the valence bond scheme starts *a priori* with poly-electronic views, thereby making visualization difficult (but not impossible). What is needed is to fix the position of one of the two electrons, and then do standard plots for the wave function as a function of the coördinates of the second electron. Thus, we plot, as an example,  $\psi_{VB}(0, 0, 0.5, 0, 0, z_2)$  vs.  $z_2$  i.e., “placing” electron 1 ( $e_1$ ) on the A nucleus (see Figure 2). We have assumed a bond length of 1 a.u.

The Maple code for this figure follows:

```
R := 1;
psi(x1,y1,z1,x2,y2,z2) := exp(-sqrt(x1^2+y1^2+(z1-R/2)^2))*
exp(-sqrt(x2^2+y2^2+(z2+R/2)^2))+exp(-sqrt(x1^2+y1^2+(z1+R/2)^2))*exp(
-sqrt(x2^2+y2^2+(z2-R/2)^2)):
```

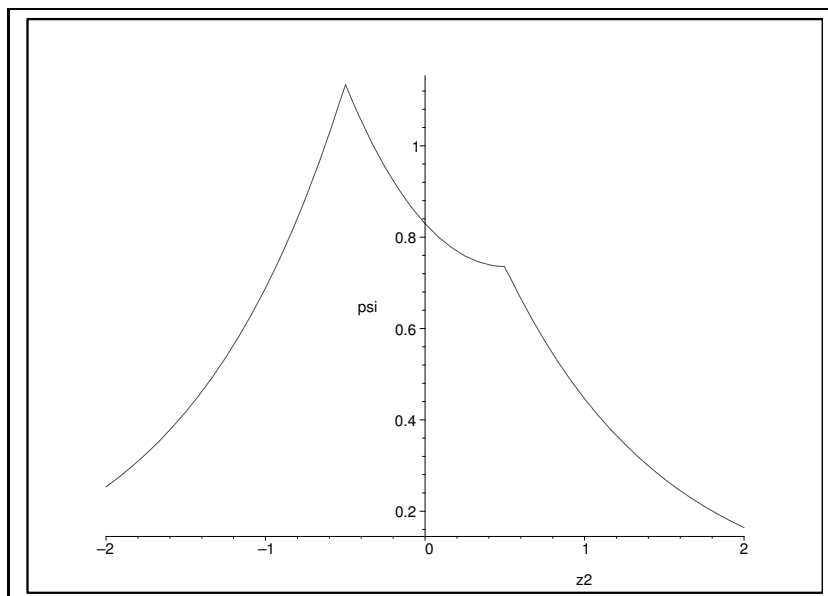


FIG. 2: Plot of  $\psi_{VB}(0, 0, 0.5, 0, 0, z)$  versus  $z_2$  (the bond line for  $e_2$ ).

```
t := subs(x1=0,x2=0,y2=0,y1=0,z1=0.5,psi(x1,y1,z1,x2,y2,z2)):
plot(t,z2=-2..2,labels=['z2','psi']);
```

The “3-dimensional” plot of the same wave function, this time as functions of  $y_2$  and  $z_2$ , is seen in Figure 3. The Maple code (continuing from the earlier code, *vide supra*.) for Figure 3 follows:

```
t2 := subs(x1=0,y1=0,z1=0.5,x2=0,psi(x1,y1,z1,x2,y2,z2)):
plot3d(t2,y2=-2..2,z2=-2..2,axes=BOXED,labels=['y2','z2','psi']);
```

and, making a 3-dimensional contour map of the highest part of this orbital, using Mathematica, we obtain Figure 4: The code for this diagram follows:

```
Needs["Graphics`ContourPlot3D`"]
R = 1.0;
LOW = -1;
HI = 1;
Psi[x1_,y1_,z1_,x2_,y2_,z2_] =
Exp[-Sqrt[x1^2+y1^2+(z1-R/2)^2]]*Exp[-Sqrt[x2^2+y2^2+(z2+R/2)^2]]+
Exp[-Sqrt[x2^2+y2^2+(z2-R/2)^2]]*Exp[-Sqrt[x1^2+y1^2+(z1+R/2)^2]];
VBvsM01=ContourPlot3D[
```

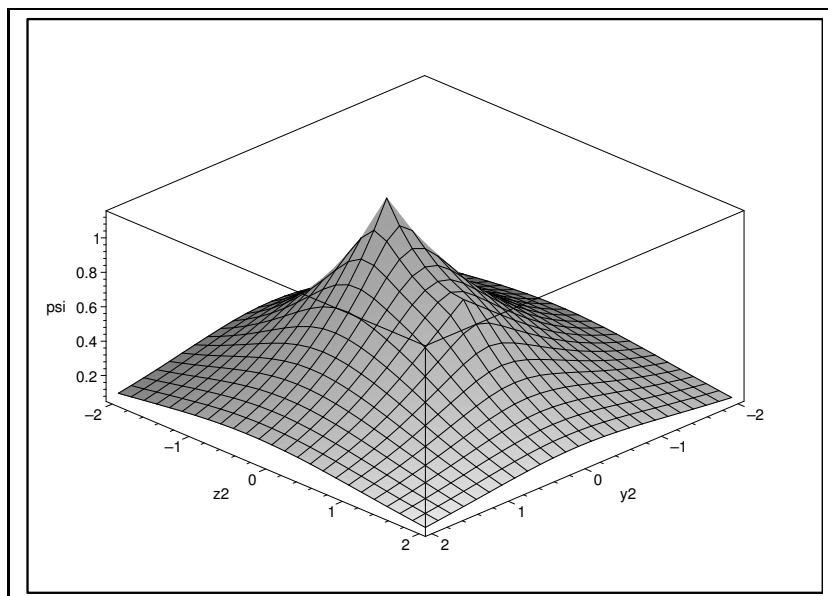


FIG. 3: 3D contour plot (Maple) for the VB wave function with electron 1 localized on the A nucleus.  $\psi_{VB}(0, 0, 0.5, 0, y_2, z_2)$  vs.  $y_2$  and  $z_2$ . The fixed electron ( $e_1$ ) is at  $(0,0,0.5)$ , i.e., the bond length for the example is 1 a.u.

```

Psi[0,0,R/2,x2,y2,z2]
,{x2,LOW,HI},
,{y2,LOW,HI},
,{z2,LOW,HI}
,Contours->{0.8},Axes->True
,AxesLabel->{"x2","y2","z2"}
,Compiled->True
,PlotPoints->{5,5,5}
]

```

Choosing a “Contours” value of 0.8 value insures that we are dealing with a small volume centered about the point  $(0,0,-R/2)$  where the electron’s wavefunction is maximum, compared to  $(0,0,R/2)$ , where the electron’s wavefunction is not so large (reflecting a repulsion between the two electrons (since electron 1 is already “located” at  $(0,0,R/2)$  for this particular plot).

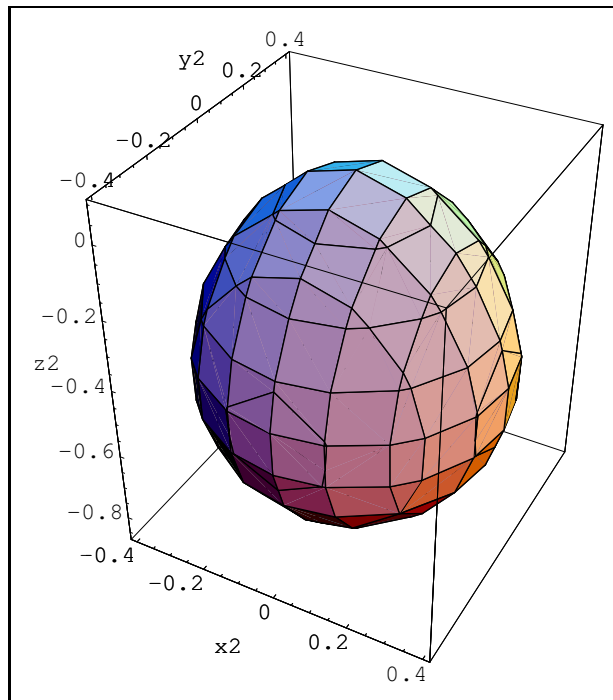


FIG. 4: This is contour drawing (3-dimensional, Mathematica) of the peak centered at  $0,0,-R/2$ . Notice the coordinate axis values.

:

### III. DISCUSSION

It is clear from the pictures that  $e_2$  is avoiding the “place” where  $e_1$  is “located”. “Placing” the electron  $e_1$  elsewhere alters the details of the plots (and one electron wavefunction fragments) but does not alter the underlying concept of avoidance shown above.

**IV. REFERENCES CITED**

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