

or more simply,

$$\mathbf{H}_e \psi_e = E_e \psi_e.$$

$\psi_e(\mathbf{r})$  is the electron wave function and  $E_e$  is the energy of the electron. The BOpp approximation to the total energy is then  $E_{tot} = E_e + E_{pp}$ .

The Born Oppenheimer model now describes an electron moving in a double well potential,

$$V_e = -(e^2/4\pi\epsilon_0)(|r_1-r|^{-1} + |r_2-r|^{-1})$$

This potential is not central - see figure 2 - so solutions will not be eigenfunctions of the angular momentum operator  $\mathbf{L}^2$ . This means the problem is still very hard.

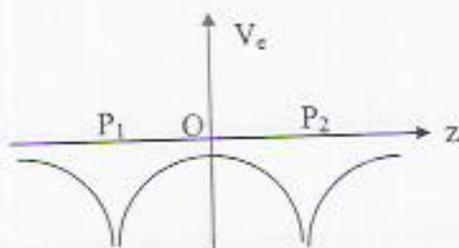


Figure 2  
The double well  
potential.

### Solutions of the Born Oppenheimer model

Although an exact solution for the ground state of the BOpp model has been found, a generally applicable approach to problems of this type is the variational method. In this scheme, a trial wavefunction with some adjustable parameter(s) is used to calculate the expectation energy:

$$E_{e,t} = (\psi_t, \mathbf{H}_e \psi_t) / (\psi_t, \psi_t)$$

$E_{e,t}$  then provides an upper bound to the true ground state energy and  $\psi_t$  is an approximation to the ground state wave function. Minimising  $E_{e,t}$  with respect to the adjustable parameters in  $\psi_t$  provides better estimates of the ground state energy, and good results can be achieved even if  $\psi_t$  is imperfect. However a sensible choice for  $\psi_t$  is important and in this case a superposition of 1s hydrogen wave functions is a good place to start. This is because when the electron is near to either proton, the system imitates a hydrogen atom and a free proton. Using  $\psi_1$  and  $\psi_2$  to denote 1s hydrogen wave functions centred on either proton then the variational choice is:

$$\psi_t = A \psi_1 + B \psi_2$$

$E_{e,t}$  is minimised at an extremum:

$$(\partial/\partial A) E_{e,t}(A,B) = (\partial/\partial B) E_{e,t}(A,B) = 0$$