PHY 308 Example Problem
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1 Bonding and Anti-bonding orbitals (10 points)

Consider the following 1D potential, 1 particle problem consisting of two δ-function potentials:

$$V(x) = -V_0\delta(x - a/2) - V_0\delta(x + a/2) \tag{1.1}$$

The potential is not unlike that an electron might feel in a diatomic molecule like H_2^+: the particle feels two centers of attraction. In case you are unfamiliar with the Dirac δ-function, they are quite useful tools for any mathematical problems involving integrals. They were invented by P. A. M. Dirac, an early pioneer in quantum mechanics, for the purpose of manipulating integrals. Mathematicians originally didn't like them (because they don't satisfy the rules of what constitutes a "function"), but eventually came around with the theory of "Generalized functions" to deal with them. The Dirac δ-function is defined as follows:

$$\delta(x) = \begin{cases} \infty, & x = 0 \\ 0, & \text{otherwise} \end{cases} \tag{1.2}$$

$$\int dx\delta(x) = 1 \tag{1.3}$$

$$\int dx\delta(x - x_0)f(x) = f(x_0) \tag{1.4}$$

The potential consisting of only one δ-function well has only one bound state. The bound solution to the 1D Time time independent Schödinger equation with one δ-function potential well, $V(x) = -V_0\delta(x)$, is given by

$$\psi_1(x) = \frac{\sqrt{mV_0}}{\hbar}\exp\left(\frac{-mV_0|x|}{\hbar^2}\right), \quad E_1 = \frac{-mV_0^2}{2\hbar^2} \tag{1.5}$$

where E is the bound state energy.

a) In the spirit of the "linear combination of atomic orbitals" (LCAO) method, use the one-well solution as a basis for the variational method to solve the double well problem. Take the basis functions two "orbitals", one centered on each well, viz. $f_1 = \psi_1(x + a/2)$, $f_2 = \psi_1(x - a/2)$.

b) Plot the ground state and excited state energy you find in a) as a function of the well separation a. You can plot energies in units of the single well energy E_1. Sketch the solutions you find for part a) for a value of $-mV_0/\hbar^2 a \approx 1/2$. Is it the lowering of the potential or kinetic energy that is most responsible for this chemical bond?

Hint: Evaluating $\langle\hat{T}\rangle$ is a little tricky because the first derivative of ψ_1 is discontinuous at $x = 0$ and the second derivative is infinite there. The integral, however, is finite (see Griffiths):

$$\lim_{\epsilon\to 0}\int_{-\epsilon}^{\epsilon} dx\frac{d^2\psi}{dx^2} = -\frac{2mV_0}{\hbar^2}\psi_1(0) \tag{1.6}$$