PHYS 451 Quantum Mechanics I (Spring 2020)
Online Quiz #6

Consider a linear triatomic molecule such as CO_2. We can create a crude model of it using the nearest neighbour approximation (just like we did in lecture 26 with a chain of 1D square wells). Note that the well in the middle (e.g. its depth and width) is different from those on the sides, because the potential due to the C atom is not the same as that due to O atoms. Determine the single-particle energy levels of CO_2 in this model. Feel free to introduce any notations you find necessary.

Solution:

Let us assume that the single-well wave functions are:
$|1\rangle = f(x+a)$ (left O atom),
$|2\rangle = g(x)$ (center C atom),
$|3\rangle = f(x-a)$ (right O atom).
Following the same approach as we adopted in lecture 26, we can seek for an approximate solution of the Schrödinger equation as a linear combination of atomic orbitals:

$$\Psi = c_1|1\rangle + c_3|3\rangle + c_3|3\rangle.$$

When the wells are sufficiently separated from each other we can disregard the overlap integrals between all atomic orbitals, i.e. we assume $\langle i|j\rangle \approx \delta_{ij}$. For the Hamiltonian matrix in basis $|j\rangle$ we have

$$\langle 1|\hat{H}|1\rangle = \langle 3|\hat{H}|3\rangle = \alpha\,,$$
$$\langle 2|\hat{H}|2\rangle = \gamma\,,$$

and, we keep the off-diagonal terms corresponding to neighbouring states

$$\langle 1|\hat{H}|2\rangle = \langle 2|\hat{H}|3\rangle = \beta\,,$$

while discarding the elements corresponding to non-neighbouring states

$$\langle 1|\hat{H}|3\rangle = 0\,.$$

Note that when the wells are sufficiently separated β is negative and $\beta \ll \alpha, \gamma$. The resulting eigenvalue problem involves a 3×3 Hamiltonian matrix:

$$\begin{pmatrix} \alpha & \beta & 0 \\ \beta & \gamma & \beta \\ 0 & \beta & \alpha \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}.$$

The solutions are

$$E_1 = \frac{\alpha+\gamma}{2} + \frac{1}{2}\sqrt{(\alpha-\gamma)^2 + 8\beta^2}\,,$$
$$E_2 = \alpha\,,$$
$$E_3 = \frac{\alpha+\gamma}{2} - \frac{1}{2}\sqrt{(\alpha-\gamma)^2 + 8\beta^2}\,.$$