

CML 100: 2017-2018
Quantum Tutorial 3

1. Identify $\hat{H}^{(0)}$, $\hat{H}^{(1)}$ and ground state $\psi^{(0)}$ and $E^{(0)}$ for the following systems
- An oscillator with potential

$$V(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 + \frac{b}{24}x^4$$

- A particle constrained to move in the region $0 < x < a$ with the potential

$$V(x) = \begin{cases} 0 & 0 \leq x < \frac{a}{2} \\ b & \frac{a}{2} < x < a \end{cases}$$

- A Helium atom
- A H-atom in an electric field of strength F . Hamiltonian for this system is

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} + eFr \cos \theta$$

- A rigid rotor with a dipole moment μ in an electric field of strength F . Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2I}\nabla^2 + \mu F \cos \theta$$

2. Using the P-I-B as the unperturbed problem, calculate the first order correction to the ground state energy for a particle constrained to move in the region $0 < x < a$ with the potential

$$V(x) = \begin{cases} 0 & 0 \leq x < \frac{a}{2} \\ b & \frac{a}{2} < x < a \end{cases}$$

3. If you use the trial function $\phi(x) = (1 + cax^2)e^{-ax^2/2}$ where $a = (k\mu/\hbar^2)$ and c is the variational parameter for the ground state energy of a Harmonic Oscillator, what do you expect the value of c should be? Why?
4. The Hamiltonian for the 3D Harmonic oscillator can be written as

$$\hat{H} = -\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{1}{2}kr^2$$

Use the trial wavefunctions $e^{-\alpha r^2}$ and $e^{-\alpha r}$ and suggest which one is better and why.

5. Apply the first order perturbation correction to He atom. Compare the results with the variational results from the lecture.
6. The Morse potential $V(x) = D(1 - e^{-\beta x})^2$ is a good approximation to the intermolecular potential energy for a diatomic molecule. The constants D and β for H_2 molecule are $D = 7.61 \times 10^{-19}$ J and $\beta = 0.0193$ pm⁻¹. Use the expansion of the exponential to see the similarity with the Anharmonic oscillator. Relate the constants D and β with those of the harmonic oscillator.

7. The P-I-B problem is fully solvable as you have seen. However, use the trial wavefunction $\phi = \sum_{n=1}^2 c_n x^n (a-x)^n$ to perform variational calculation for the ground state and compare the results. Is the trial function well-behaved?
8. The spin operators also obey the commutation relations

$$[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z; \quad [\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x; \quad [\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y$$

We define $\hat{S}_+ = \hat{S}_x + i\hat{S}_y$ and $\hat{S}_- = \hat{S}_x - i\hat{S}_y$.

- (a) Show that \hat{S}_+ and \hat{S}_- are non-Hermitian.
- (b) Show that $[\hat{S}_z, \hat{S}_+] = \hbar\hat{S}_+$ and $[\hat{S}_z, \hat{S}_-] = -\hbar\hat{S}_-$
- (c) Show that $\hat{S}_+\hat{S}_- = \hat{S}^2 - \hat{S}_z^2 + \hbar\hat{S}_z$ and $\hat{S}_-\hat{S}_+ = \hat{S}^2 - \hat{S}_z^2 - \hbar\hat{S}_z$
Where, $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$
- (d) What is the result of operating \hat{S}_+ and \hat{S}_- on the two spins α and β ?
9. The total z component of the spin angular momentum operator for an N-electron system is

$$\hat{S}_{z,total} = \sum_{j=1}^N \hat{S}_{z,j}$$

Show that

$$\psi = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) \end{vmatrix}$$

is an eigenfunction of $\hat{S}_{z,total}$.

10. Use the z-axis as the internuclear axis and evaluate the overlap integral for an 1s-orbital on one H-atom and a 2p_x orbital on the other H-atom. (Hint: You need not solve any integrals).
11. Determine the M.O.'s for 1,3-butadiene using the Hückel MOT. Sketch the MOs showing the size of the p-orbitals on the four carbon atoms proportional to the coefficients.
12. Calculate the delocalization energy for benzene and M.O.s. Sketch the M.O.s.