Quantum Mechanics and Spectroscopy
CHEM 3PA3
Tutorial 2

1. If we have a cubic box with four electrons, and assuming that the electron-electron repulsion between them can be neglected, what would be the ground state energy of the four electron system?

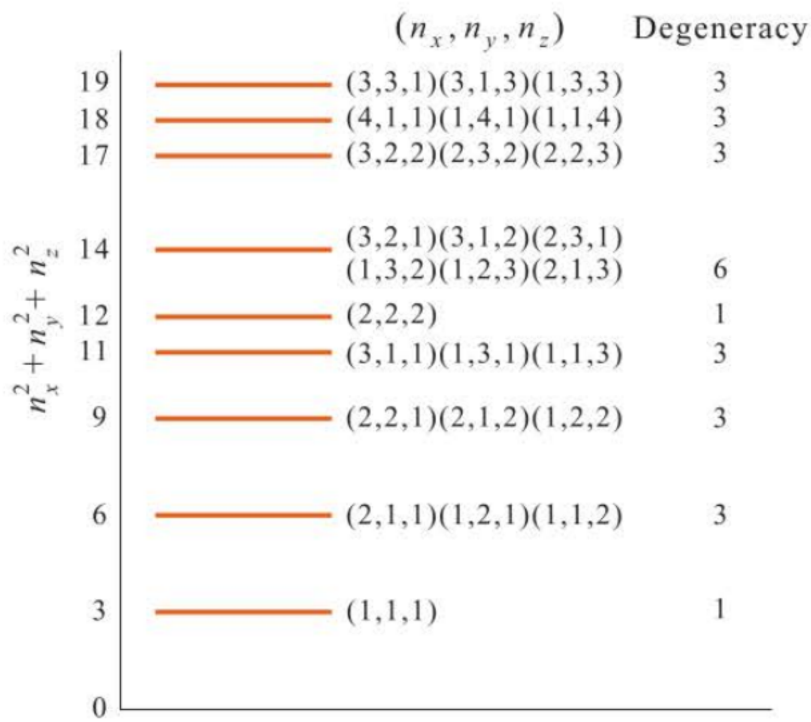

Figure 1: The energy levels for a particle in a cubic box. Notice that the energy levels get closer as the quantum numbers increase.

The ground state energy is given by the sum of two electron occupying the $(1, 1, 1)$ state and two electron occupying any of the three possible orbitals $(2, 1, 1), (1, 2, 1)$, and $(1, 1, 2)$.

$$E = 2 \times E_{111} + 2 \times E_{112} = 2 \times \frac{3h^2}{8ma^2} + 2 \times \frac{6h^2}{8ma^2} = \frac{9h^2}{4ma^2}.$$

2. What is the degeneracy of the ground state energy for this system?

The $(1, 1, 1)$ orbital will be occupied, but the three degenerate spatial orbitals will only be occupied by two electrons. Neglecting the electron-electron interaction implies that the electrons can go into the same spatial orbital, even if this does not maximize multiplicity. Taking spin into consideration, there are six spatial orbitals and only two of them will be occupied. Therefore the degeneracy is given by $\binom{6}{2} = 15$.

3. Write a possible Slater determinant for this system.

$$\Psi = \frac{1}{(4!)^{1/2}} \begin{bmatrix} \Psi_{111}(\mathbf{r}_1)\alpha(1) & \Psi_{111}(\mathbf{r}_1)\beta(1) & \Psi_{112}(\mathbf{r}_1)\alpha(1) & \Psi_{112}(\mathbf{r}_1)\beta(1) \\ \Psi_{111}(\mathbf{r}_2)\alpha(2) & \Psi_{111}(\mathbf{r}_2)\beta(2) & \Psi_{112}(\mathbf{r}_2)\alpha(2) & \Psi_{112}(\mathbf{r}_2)\beta(2) \\ \Psi_{111}(\mathbf{r}_3)\alpha(3) & \Psi_{111}(\mathbf{r}_3)\beta(3) & \Psi_{112}(\mathbf{r}_3)\alpha(3) & \Psi_{112}(\mathbf{r}_3)\beta(3) \\ \Psi_{111}(\mathbf{r}_4)\alpha(4) & \Psi_{111}(\mathbf{r}_4)\beta(4) & \Psi_{112}(\mathbf{r}_4)\alpha(4) & \Psi_{112}(\mathbf{r}_4)\beta(4) \end{bmatrix}$$

4. For $\hat{A} = x^2$ and $\hat{B} = \frac{d}{dx}$, show that $\hat{A}\hat{B}f(x) \neq \hat{B}\hat{A}f(x)$.

$$\hat{A}\hat{B}f(x) = x^2\frac{df}{dx}$$
$$\hat{B}\hat{A}f(x) = \frac{d}{dx}\left[x^2 f(x)\right] = 2xf(x) + x^2\frac{df}{dx}$$
$$\hat{A}\hat{B}f(x) \neq \hat{B}\hat{A}f(x)$$

$\hat{A}$ and $\hat{B}$ do not commute, $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \neq 0$.

5. Given the following Hamiltonian and ground state wavefunction for a certain system,

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$
$$\Psi_0(x) = A\exp\left(-\frac{\sqrt{km}}{2\hbar}x^2\right)$$

- What is the normalization constant for the wavefunction?

$$\int_{-\infty}^{\infty} \Psi_0^\star(x)\Psi_0(x)\,\mathrm{d}x = 1 \tag{1}$$
$$\int_{-\infty}^{\infty} A^2\exp\left(-\frac{\sqrt{km}}{\hbar}x^2\right)\mathrm{d}x = 1 \tag{2}$$
$$A^2\left(\frac{\pi}{\sqrt{km}/\hbar}\right)^{1/2} = 1 \tag{3}$$
$$A = \left(\frac{\pi}{\sqrt{km}/\hbar}\right)^{1/4} \tag{4}$$

- What is the ground state energy of the system?

$$\int_{-\infty}^{\infty} \Psi_0^\star(x) \hat{H} \Psi_0(x)\,\mathrm{d}x$$

$$= \int_{-\infty}^{\infty} A \exp\left(-\frac{\sqrt{km}}{2\hbar}x^2\right)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right] A \exp\left(-\frac{\sqrt{km}}{2\hbar}x^2\right)\mathrm{d}x$$

$$= A^2 \left\{-\frac{\hbar^2}{2m}\int_{-\infty}^{\infty} \exp\left(-\frac{\sqrt{km}}{2\hbar}x^2\right)\left[\frac{d^2}{dx^2}\right]\exp\left(-\frac{\sqrt{km}}{2\hbar}x^2\right)\mathrm{d}x \right.$$

$$\left. + \frac{1}{2}k\int_{-\infty}^{\infty} \exp\left(-\frac{\sqrt{km}}{2\hbar}x^2\right)x^2 \exp\left(-\frac{\sqrt{km}}{2\hbar}x^2\right)\mathrm{d}x\right\}$$

$$= A^2 \left\{-\frac{\hbar^2}{2m}\left(-\frac{\sqrt{km}}{\hbar}\right)\int_{-\infty}^{\infty} \exp\left(-\frac{\sqrt{km}}{2\hbar}x^2\right)\frac{d}{dx}\left[x\exp\left(-\frac{\sqrt{km}}{2\hbar}x^2\right)\right]\mathrm{d}x \right.$$

$$\left. + \frac{1}{2}k\int_{-\infty}^{\infty} x^2 \exp\left(-\frac{\sqrt{km}}{\hbar}x^2\right)\mathrm{d}x\right\}$$

$$= A^2 \left\{-\frac{\hbar^2}{2m}\left(-\frac{\sqrt{km}}{\hbar}\right)\int_{-\infty}^{\infty} \exp\left(-\frac{\sqrt{km}}{2\hbar}x^2\right)\left[\exp\left(-\frac{\sqrt{km}}{2\hbar}x^2\right)\right]\mathrm{d}x \right.$$

$$- \frac{\hbar^2}{2m}\left(-\frac{\sqrt{km}}{\hbar}\right)^2\int_{-\infty}^{\infty} \exp\left(-\frac{\sqrt{km}}{2\hbar}x^2\right)\left[x^2\exp\left(-\frac{\sqrt{km}}{2\hbar}x^2\right)\right]\mathrm{d}x$$

$$\left. + \frac{1}{2}k\int_{-\infty}^{\infty} x^2 \exp\left(-\frac{\sqrt{km}}{\hbar}x^2\right)\mathrm{d}x\right\}$$

$$= A^2 \left\{\left(\frac{\hbar k^{1/2}}{2m^{1/2}}\right)\int_{-\infty}^{\infty} \exp\left(-\frac{\sqrt{km}}{\hbar}x^2\right)\mathrm{d}x\right\} = \frac{\hbar k^{1/2}}{2m^{1/2}}$$