General Chemistry I

단원	Ch 4. Introduction to Quantum Mechanics
학습 주제	Complicated problems

2D, 3D PiB

4.6.2 Energy Levels for Particles in Two- and Three-Dimensional Boxes

The Schrödinger equation is readily generalized to describe a particle in a box of two or three dimensions. A particle in a two-dimensional box can be visualized as a marble moving in the x-y plane at the bottom of a deep elevator shaft, with infinite potential walls confining its motion in the x and y directions. A particle in a three-dimensional rectangular box has infinite potential walls confining its motion in the x, y, and z directions. In both cases, the potential energy function is zero throughout the interior of the box. The wave function ψ and potential V now depend on as many as three coordinates (x, y, z), and derivatives with respect to each coordinate appear in the Schrödinger equation. Because the potential energy is constant in all directions inside the box, the motions in the x direction are independent of the motions in the y and z directions, and vice versa. For potential functions of this type, the Schrödinger equation can be solved by the method of *separation of variables*, and the results are quite interesting. The wave function is the product of the wave functions for independent motion in each direction, and the energy is the sum of the energies for independent motion in each direction. Therefore, we can immediately apply the results for the one-dimensional motions developed earlier to discuss, in turn, the energies and wave functions for multidimensional boxes.

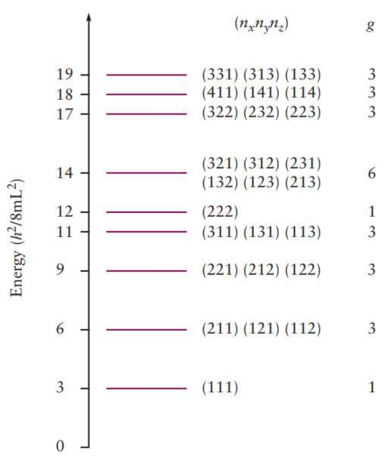
The allowed energies for a particle in a three-dimensional rectangular box are

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right] \qquad \begin{cases} n_x = 1, 2, 3, \ldots \\ n_y = 1, 2, 3, \ldots \\ n_z = 1, 2, 3, \ldots \end{cases} \qquad [4.39]$$

where L_x, L_y, and L_z are the side lengths of the box. Here the state is designated by a set of three quantum numbers, (n_x, n_y, n_z). Each quantum number ranges independently over the positive integers. We can obtain the energy levels for a particle in a two-dimensional box in the x-y plane from Equation 4.39 by setting $n_z = 0$ and restrict the box to be a square by setting $L_x = L_y = L$. Similarly, we can specialize Equation 4.39 to a cubic box by setting $L_x = L_y = L_z = L$.

$$E_{n_x n_y n_z} = \frac{h^2}{8mL^2}\left[n_x^2 + n_y^2 + n_z^2\right] \qquad \begin{cases} n_x = 1, 2, 3, \ldots \\ n_y = 1, 2, 3, \ldots \\ n_z = 1, 2, 3, \ldots \end{cases} \qquad [4.40]$$

FIGURE 4.41 The energy levels for a particle in a cubic box. The quantum numbers identifying the quantum states and the degeneracy values are given for each energy level.



[Example 4.7] 다음 두 계를 생각하자. (1) 길이가 1.0Å인 1차원 상자 속의 전자 그리고 (2) 변의 길이가 30CM인 정육면체 상자 속의 헬륨 원자. 바닥 상태와 첫 번째 들뜬 상태 간의 에너지 차이를 계산하고 에너지를 kJ/mol 단위로 표시하라.

4.7.1 Wave Functions for Particles in Square Boxes

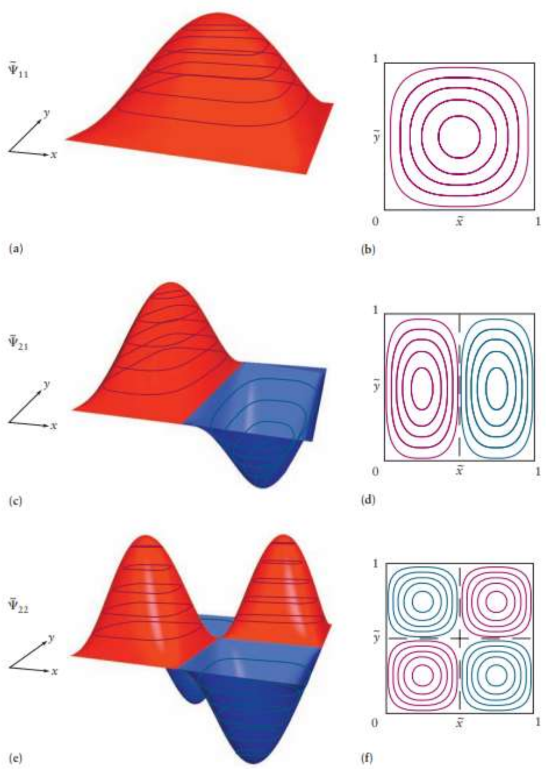
The wave function for a particle in a square box of length L on each side in the x-y plane, which we denote as Ψ, is given by

$$\Psi_{n_x n_y}(x,\ y) = \psi_{n_x}(x)\psi_{n_y}(y) = \frac{2}{L}\ \sin\left(\frac{n_x \pi x}{L}\right)\ \sin\left(\frac{n_y \pi y}{L}\right) \qquad [4.41]$$

as explained earlier. To generate a graphical representation, we calculate the value of Ψ at each point (x, y) in the plane and plot this value as a third dimension above the x-y plane. To make our graphs apply to square boxes of any size, we show them for dimensionless variables $\tilde{x} = x/L$ and $\tilde{y} = y/L$, which range from 0 to 1. We also plot the value of the wave function as a dimensionless function $\tilde{\Psi}$, defined as the ratio of the value of Ψ to its maximum value, $\tilde{\Psi}(\tilde{x}, \tilde{y}) = \Psi(\tilde{x}, \tilde{y})/\Psi_{\max}$. The value of $\tilde{\Psi}$ ranges from -1 to 1. We show three examples in Figure 4.42.

The wave function for the ground state $\tilde{\Psi}_{11}(\tilde{x},\ \tilde{y})$ (see Fig. 4.42a) has no nodes and has its maximum at the center of the box, as you would expect from the one-dimensional results in Figure 4.37 from which $\tilde{\Psi}_{11}(\tilde{x},\ \tilde{y})$ is constructed.

FIGURE 4.42 Wave function for a particle in a square box in selected quantum states. Dimensionless variables are used. (a) Three-dimensional plot for the ground state $\tilde{\Psi}_{11}(\tilde{x}, \tilde{y})$. (b) Contour plot for $\tilde{\Psi}_{11}(\tilde{x}, \tilde{y})$. (c) Three-dimensional plot for the first excited state $\tilde{\Psi}_{21}(\tilde{x}, \tilde{y})$. (d) Contour plot for $\tilde{\Psi}_{21}(\tilde{x}, \tilde{y})$. (e) Three-dimensional plot for the second excited state $\tilde{\Psi}_{22}(\tilde{x}, \tilde{y})$. (f) Contour plot for $\tilde{\Psi}_{22}(\tilde{x}, \tilde{y})$.



4.7.2 Wave Functions for Particles in Cubic Boxes

The wave function for a particle in a cubic box of length L on each side, with one corner located at the origin of coordinates, is given by

$$\Psi_{n_x n_y n_z}(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \qquad [4.42]$$

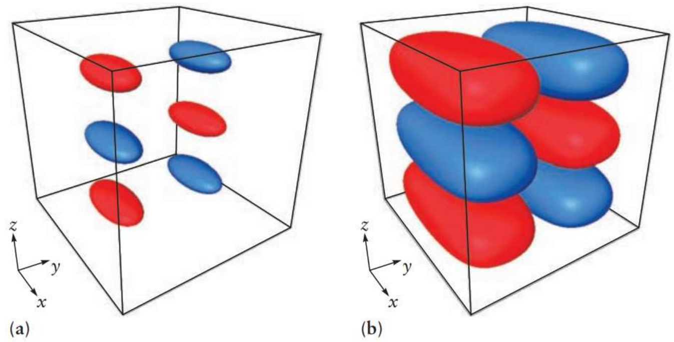


FIGURE 4.44 Isosurfaces for $\tilde{\Psi}_{123}(\tilde{x}, \tilde{y}, \tilde{z})$ for a particle in a cubic box. (a) Isosurfaces for wave function value $\tilde{\Psi}_{123} = \pm 0.8$. (b) Isosurfaces for wave function value $\tilde{\Psi}_{123} = \pm 0.2$. Each isosurface is shown in the same color as the corresponding contour in Figure 4.43.

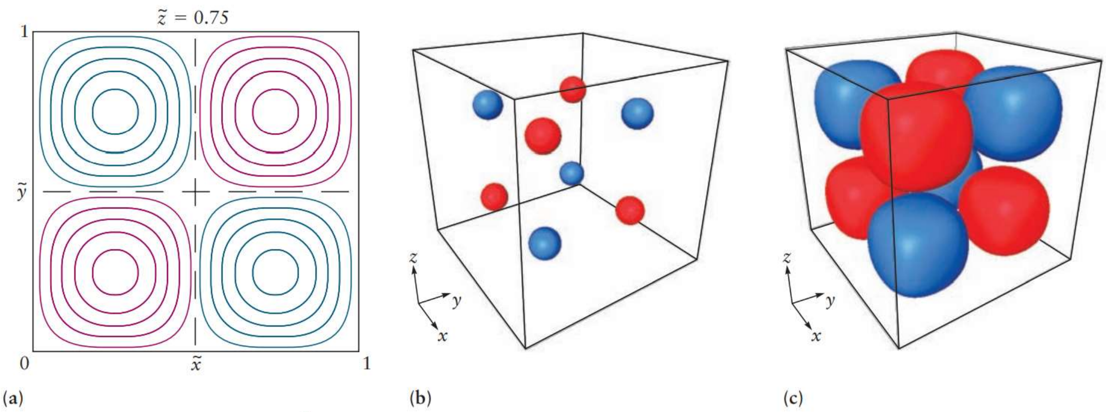
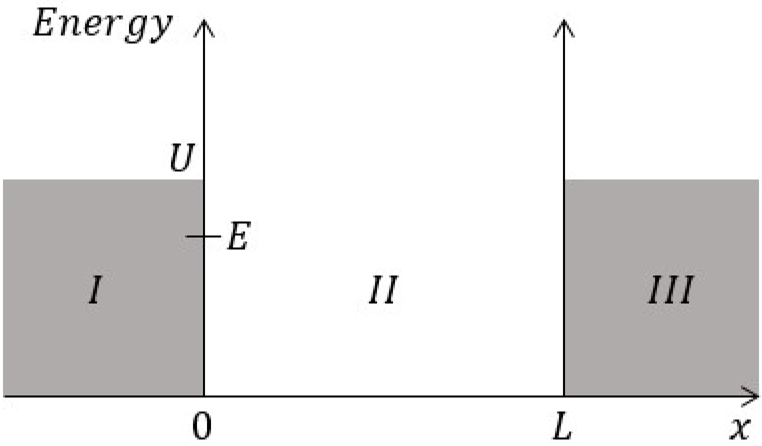


FIGURE 4.45 Representations of $\tilde{\Psi}_{222}(\tilde{x}, \tilde{y}, \tilde{z})$ for a particle in a cubic box. (a) Contour plots for a cut taken at $\tilde{z} = 0.75$. (b) Isosurfaces for wave function value $\tilde{\Psi}_{222} = \pm 0.9$. (c) Isosurfaces for wave function value $\tilde{\Psi}_{222} = \pm 0.3$. Each isosurface is shown in the same color as the corresponding contour in (a).

41. Write the wave function $\tilde{\Psi}_{12}(\tilde{x}, \tilde{y})$ for a particle in a square box.
- **(a)** Convince yourself it is degenerate with $\tilde{\Psi}_{21}(\tilde{x}, \tilde{y})$.
- **(b)** Convince yourself that its plots are the same as those of $\tilde{\Psi}_{21}(\tilde{x}, \tilde{y})$ rotated by 90 degrees in the x-y plane.
- **(c)** Give a physical explanation why the two sets of plots are related in this way.

42. Write the wave function for the highly excited state $\tilde{\Psi}_{100,100}(\tilde{x}, \tilde{y})$ for a particle in a square box.
- **(a)** Determine the number of nodal lines and the number of local probability maxima for this state.
- **(b)** Describe the motion of the particle in this state.

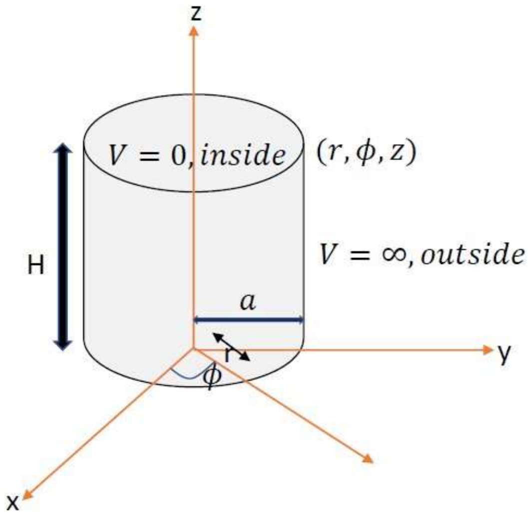
유한 퍼텐셜 문제 풀어라.



참고 : https://url.kr/3gudmi(상) https://url.kr/3pqnfi(하)

$$U=\begin{cases} V_0\ (|x|>a) \\ 0\ \ (|x|<a) \end{cases}$$

2차원 Cylindrical Infinite potential wall 문제 풀어라.



참고 : https://url.kr/bxufzv

Problem Set 5 : 예제, 그림 해석(등고면 그림)