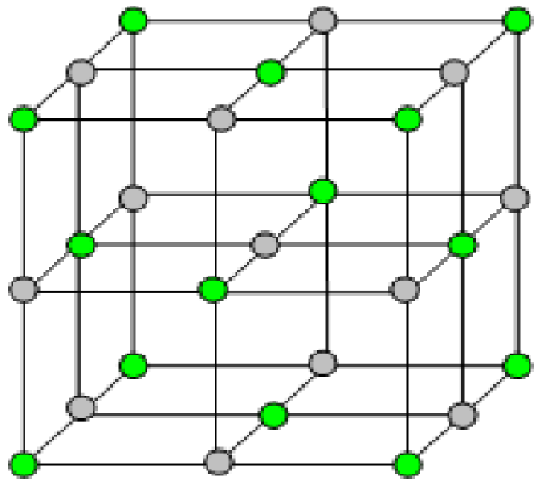
Chap. 1-2
Chemical Bonding of Atom

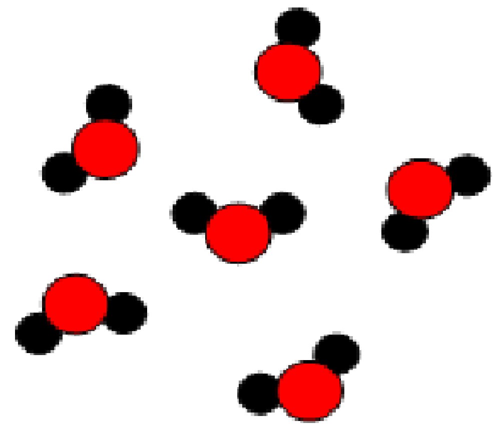
Compounds, Ions, and Molecules

- An element is a type of matter which is in its simplest form composed of only one type of atom. A compound is a sample of matter that contains two or more elements chemically combined to form a new substance. There are two fundamental types of compounds: ionic and molecular.

- Ionic compounds are composed of positively and negatively charged ions held together by electrostatic attractions casually referred to as 'ionic bonds.'
- Molecular compounds are composed of molecules, which are groups of atoms joined together by pairs of shared electrons. Solid ionic compounds do not contain molecules. Instead, because opposite charges attract one another, the ions stack themselves in crystals such that positive ions are surrounded by negative ions, and vice versa.



An ionic compound has alternating positively and negatively charged particles in a pattern that extends in all three dimensions.



A molecular compound has discrete groups of atoms joined together to form molecules.

The Chemical Bond

- A bond is the interaction between two or more atoms that allows them to form a substance different from the independent atoms. This interaction involves the outer electrons of the atoms. These electrons are transferred from one atom to another or shared between them. Bonds may be between atoms of different elements to make a compound, like the two hydrogen atoms and one oxygen atom in a water molecule. But bonds can also be between atoms of a single element. Bonds can be interactions between a few atoms, as in a molecule of water or sulfur. However, bonds may hold hundreds or thousands of atoms together to form a large molecule like insulin or DNA.
- There are three fundamental categories of bonds: ionic, covalent, and metallic.
- Ionic bonds : electrostatic attractions between oppositely charged particles more properly referred to as ionic structure.
- Covalent bonds : pairs of electrons that are shared more or less evenly between two atoms.
- Metallic bonds : loosely held outer electrons surrounding packed cations. Metallic bonds are most important in understanding the properties of pure metallic elements and in mixtures of metals (alloys) rather than in compounds, so we will save the discussion of metallic bonds for later.

Octet formulation

- The **octet rule** is a chemical rule of thumb that states that atoms tend to combine in such a way that they each have eight electrons in their valence shells, giving them the same electronic configuration as a noble gas. The rule is applicable to the main-group elements, especially carbon, nitrogen, oxygen, and the halogens, but also to metals such as sodium or magnesium. In simple terms, molecules or ions tend to be most stable when the outermost electron shells of their constituent atoms contain eight electrons.

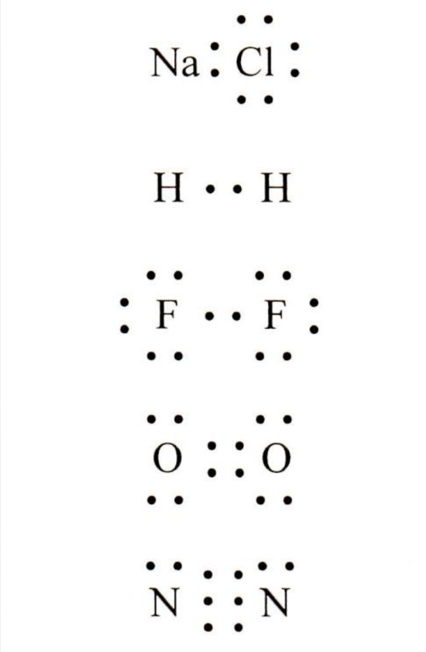


그림 1-17 8중 공식이 적용된 결합의 예.

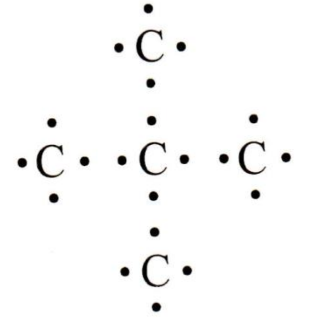


그림 1-18 탄소의 공유 결합.

Ionic Bonds

- **Ionic compounds** in the solid state are held together by electrostatic attractions between opposite charges. Sodium chloride (table salt), silver sulfide (silver tarnish), and hydrated iron (III) oxide (rust) are examples of ionic compounds.
- In a compound like silver sulfide, the individual silver atoms have lost electrons and the sulfur atoms have gained electrons. These ions interact to form a solid compound because opposite ions attract one another. When a silver spoon tarnishes, the silver atoms lose electrons to the sulfur atoms in sulfur oxides in the air. This chemical process is called oxidation/reduction. The same compound can also be formed if we mix an aqueous solution of silver nitrate with an aqueous solution of sodium sulfide. This chemical process is called metathesis. In both cases, silver sulfide ionic compound is formed.
- Is there such thing as a silver sulfide molecule? The answer to this question depends on who you ask. Most chemistry text books refer to the attractions between oppositely charged ions as 'ionic bonds' yet qualify this as referring to the forces that are involved in the formation of the overall three dimensional structure of an ionic crystal. Certainly, there isn't anything similar to a molecule inside an ionic crystal.

Energy change in the ionization process

- The formation of an ionic bond proceeds when the cation, whose ionization energy is low, releases some of its electrons to achieve a stable electron configuration. The anion, whose electron affinity is positive, then accepts the electrons, again to attain a stable electron configuration. Typically, the stable electron configuration is one of the noble gases for elements in the s-block and the p-block, and particular stable electron configurations for d-block and f-block elements. The electrostatic attraction between these two entities forms the ionic bond.

$$K + Cl \rightarrow K^+ + e^- + Cl - 4.34\ \text{eV}$$

$$Cl + e^- \rightarrow Cl^- + 3.82\ \text{eV}$$

$$K + Cl \rightarrow K^+ + Cl^- - 0.52\ \text{eV}$$

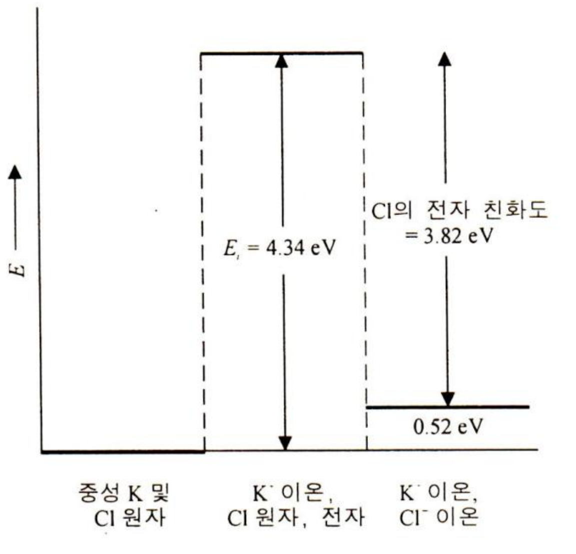


그림 1-19 KCl 의 이온화 과정에 따른 에너지 변화.

The potential energy between ions

The coulombic potential energy between ions

$$E_a = -\frac{Ae^2}{r} \qquad \text{(A : constant)} \qquad (1\text{-}49)$$

As the ions close to each other,
the repulsion energy between electrons will be

$$E_r = \frac{B}{r^n}$$

The total potential energy
of the ionic bonding

$$E_p = -\frac{Ae^2}{r} + 0.52\ \text{eV} + \frac{B}{r^n}$$

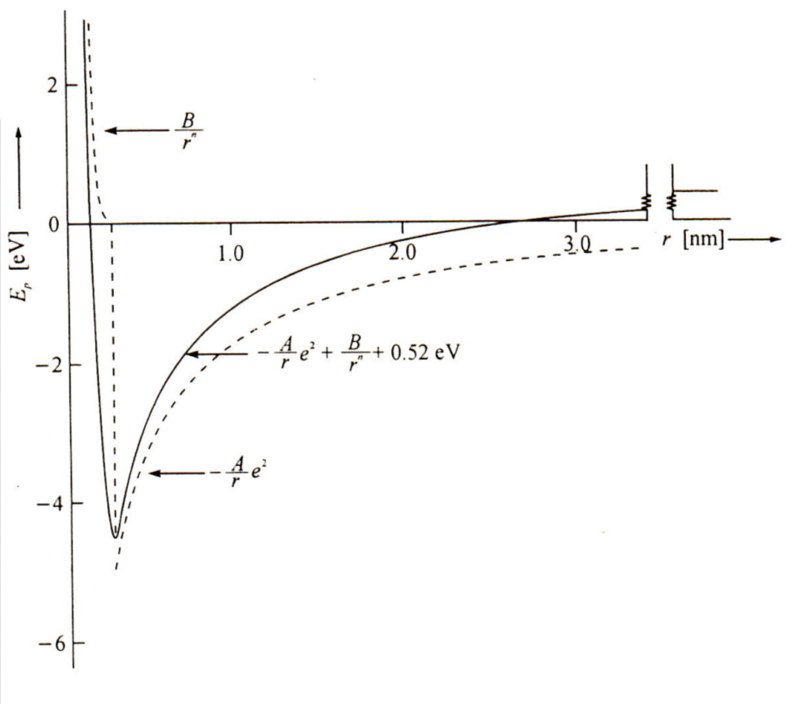


그림 1-20 이온간 간격 r에 따른 K^+와 Cl^-의 전체 에너지.

To calculate the total potential energy

The repulsion energy between ith and jth ions

$$\frac{be^2}{r_{ij}{}^n} \qquad (1\text{-}53)$$

The coulombic potential energy between ith and jth ions

$$\pm \frac{\nu_i \nu_j e^2}{r_{ij}} \qquad (1\text{-}54)$$

The total potential energy at the origin ion due to jth ions

$$\phi_{0,j} \equiv \phi_j = \frac{be^2}{r_j{}^n} \pm \frac{\nu^2 e^2}{r_j} \qquad (1\text{-}55)$$

$$r_j = p_j r_1 \qquad (1\text{-}56)$$

The total potential energy at the origin ion due to all ions

$$\phi = \sum_{j=1}^{N} \phi_j = \frac{be^2}{(r_1)^n}\left(\sum_j \frac{1}{p_j{}^n}\right) - \frac{\nu^2 e^2}{r_1}\left(\sum_j (\mp)\frac{1}{p_j}\right) \qquad (1\text{-}57)$$

$$= \frac{B_1 e^2}{(r_1)^n} - \frac{A_1 \nu^2 e^2}{r_1}$$

$$\phi = \sum_{j=1}^{N} \phi_j = \frac{be^2}{(r_1)^n}\left(\sum_j \frac{1}{p_j{}^n}\right) - \frac{\nu^2 e^2}{r_1}\left(\sum_j (\mp)\frac{1}{p_j}\right)$$

$$= \frac{B_1 e^2}{(r_1)^n} - \frac{A_1 \nu^2 e^2}{r_1} \quad (1\text{-}57)$$

Pauli's repulsion term

$$B_1 = \sum_j \frac{1}{p_j{}^n} \quad (1\text{-}58)$$

Madelung constant

$$A_1 = \sum_j (\mp)\frac{1}{p_j} \quad (1\text{-}59)$$

표 1-7 마델룽 상수.

결정 구조	마델룽 상수
염화나트륨 구조(NaCl)	1.74756
염화세슘 구조(CsCl)	1.76267
스팔러라이트 구조(α-ZnS)	1.63806
우르짜이트 구조(β-ZnS)	1.64132
불화칼슘 구조(CaF_2)	5.03878

원점 이온에 대한 전체 퍼텐셜 에너지는

$$\phi = \frac{B_1 e^2}{(r_1)^n} - \frac{A_1 v^2 e^2}{r_1} \tag{1-60}$$

이므로 윗식에서 모르는 변수는 B_1과 n이다. 퍼텐셜 에너지가 최소가 될 때는

$$\frac{d\phi}{dr_1} = -n\frac{B_1 e^2}{r_1^{n+1}} + \frac{A_1 v^2 e^2}{r_1^2} = 0 \tag{1-61}$$

이므로 여기에서 변수 B_1은

$$B_1 = \frac{v^2 A_1}{n} r_0^{\,n-1} \tag{1-62}$$

가 되어 변수 B_1을 구할 수 있다. 여기서 r_0는 평형 이온간 거리이다. 이 평형 이온간 거리는

$$r_0 = \left[\frac{nB_1}{v^2 A_1}\right]^{\frac{1}{n-1}} \tag{1-63}$$

로 표시할 수 있다. B_1을 식 (1-60)에 대입하여 평형 이온간 거리에서 원점 이온에 대한 퍼텐셜 에너지를 구하면

$$\phi_0 = -\frac{A_1 v^2 e^2}{r_0}\left(1-\frac{1}{n}\right) \tag{1-64}$$

가 나온다.

결정 전체인 N개의 이온에 대한 응집 에너지는

$$\frac{N}{2}\phi_0 = -\frac{N}{2}\frac{A_1 v^2 e^2}{r_0}\left(1-\frac{1}{n}\right) \tag{1-65}$$

공유 결합은 전기 음성도가 큰 비금속 원자들이 주로 갖는 결합의 형태이다. 이온 결합에서 이온이 안정된 꽉 찬 껍질 배치를 만들기 위해 전자를 주고 받는 것과 마찬가지로 공유 결합에서 원자는 전자를 서로 공유함으로써 채워진 전자 껍질 배치를 만든다. 대칭을 고려하면 같은 원소로 이루어진 두 원자 사이에서는 전자가 한쪽으로 이동하여 극성이 되는 이온 결합이 될 수가 없고, 대신에 비극성의 공유 결합이 형성된다. 안정된 꽉 찬 껍질의 전자 배치를 하기 위해서는 공유하는 전자를 포함하여 He, Ne, Ar, Kr, Xe, Rn 등의 전자 배치를 하여야 한다. 따라서 공유를 하기 위해 추가로 필요한 전자의 숫자는 앞에서 설명한 8 중 공식에서 얻어진다.

이와 같이 공유 결합에서는 결합을 형성하기 위해 적어도 하나의 반만 차 있는 궤도(half-filled orbital)가 존재하는 것이 필수조건이다. 반만 차 있는 궤도가 있을 경우에 다른 원자에서 하나씩의 결합 전자를 얻어 결합을 형성할 수 있기 때문이다. 일반적으로 반만 차 있는 궤도의 수와 결합의 수는 같다.

The Covalent Bond

- **Electronegativity and Bonding**
- Covalent bonds are pairs of electrons shared between two atoms in a molecule. Pure covalent (also called non-polar) bonds are ones in which both atoms share the electrons evenly. By evenly, we mean that the electrons have an equal probability of being at a certain radius from the nuclei of either atom. Polar covalent bonds are ones in which the electrons have a higher probability of being in the proximity of one of the atoms.
- A pure covalent or non-polar bond has difference of about 0.5 or less in the electronegativities of the two atoms. A pure covalent bond can form between two atoms of the same element (such as in diatomic oxygen molecule) or atoms of different elements that have similar electronegativies (such as in the carbon and hydrogen atom in methane). A polar covalent bond is a pair of electrons shared between two atoms with significantly different electronegativities (from about 0.5 to 2.0 difference). These bonds tend to form between highly electronegative non-metals and other non-metals, such as the bond between hydrogen and oxygen in water.

- In compounds that have elements with very different electronegativities (greater than 2.0 difference), the electrons can be considered to have been transferred to form ions. We classify these compounds as being ionic. In the gas phase, pairs of these ions have electron densities similar to extremely polar bonds. This brings up the philosophical question of whether or not there is a fundamental difference between ionic and covalent compounds on the very smallest level (one more time we're asking if there is such a thing as a silver sulfide molecule!). Many chemists prefer to call the attraction between oppositely charged ions in an ionic crystal an 'ionic structure' and reserve the word 'bond' for shared electrons. In that case, small clusters of gaseous ions have pairs of shared electrons and can be thought of as molecules, but solid ionic crystals do not.

반만 차 있는 궤도의 수와 결합의 수가 항상 일치하는 것은 아니다. 탄소(Z = 4, IV족)는 $1s^22s^22p^2$로 2 개의 반만 차 있는 궤도를 가지고 있으나, 다이아몬드나 CH_4에서는 동등한 강도의 결합이 4 개 형성된다. 탄소에서 4 개의 결합이 형성되는 것을 설명하기 위해 2s에 있는 전자 하나가 2p 궤도로 올라간다고 생각한다(그림 1-21).

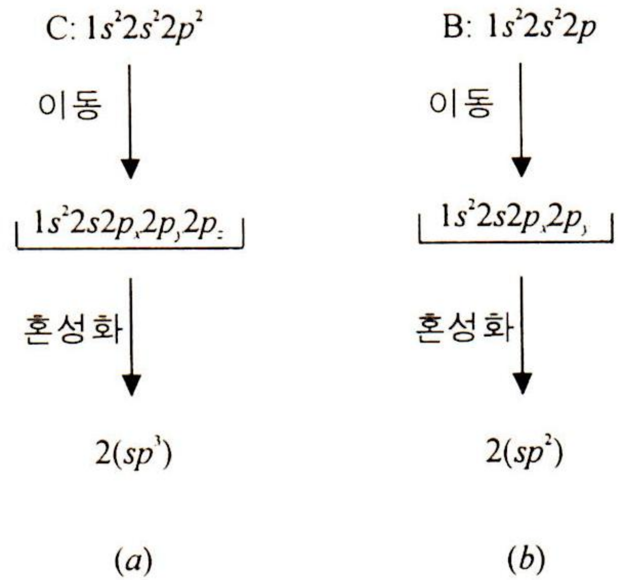


그림 1-21 C와 B에서 혼성화가 일어나는 과정을 나타낸 그림.

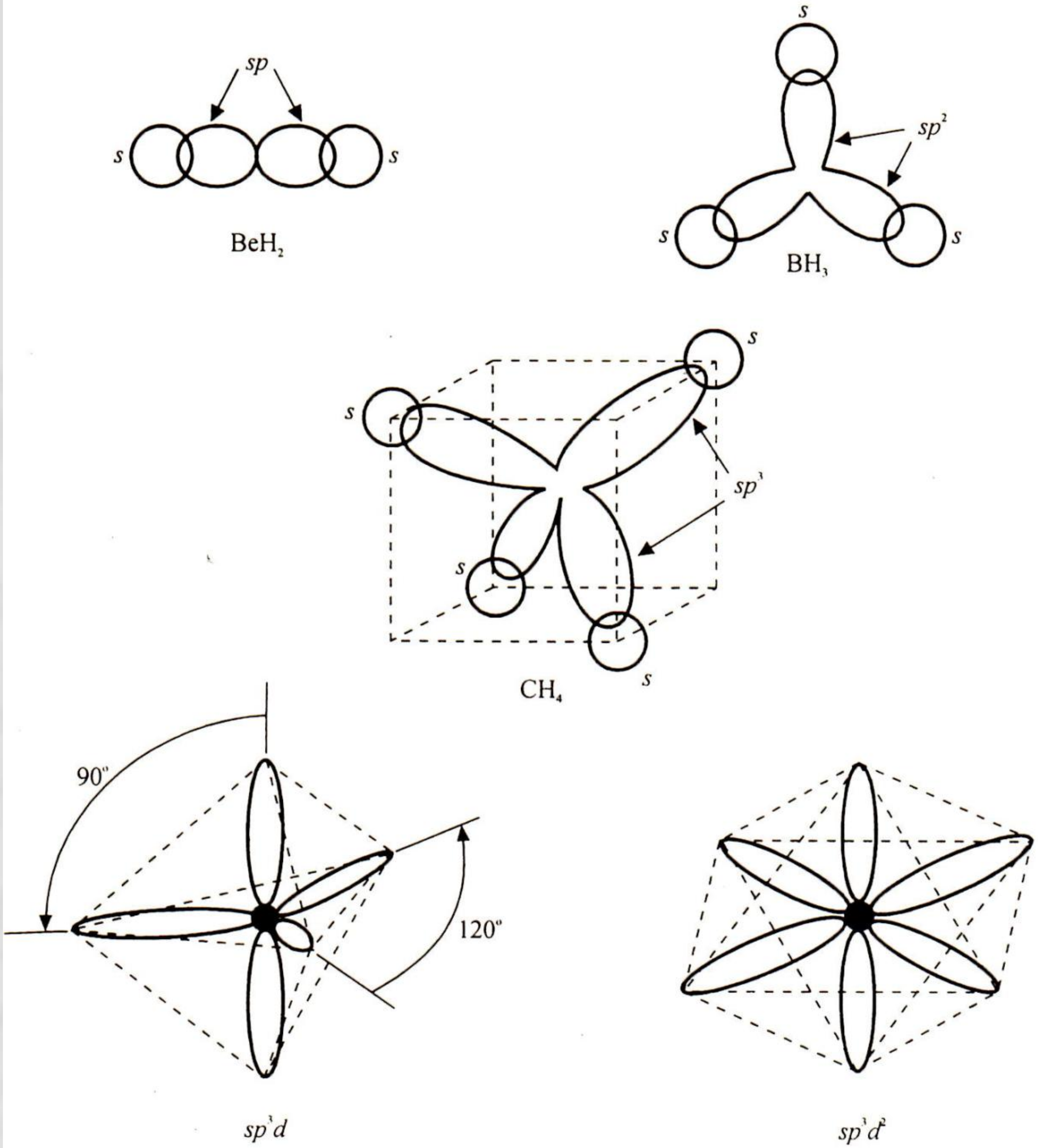


그림 1-22 sp, sp^2, sp^3, sp^3d, sp^3d^2 혼성 궤도의 기하학적인 모양.

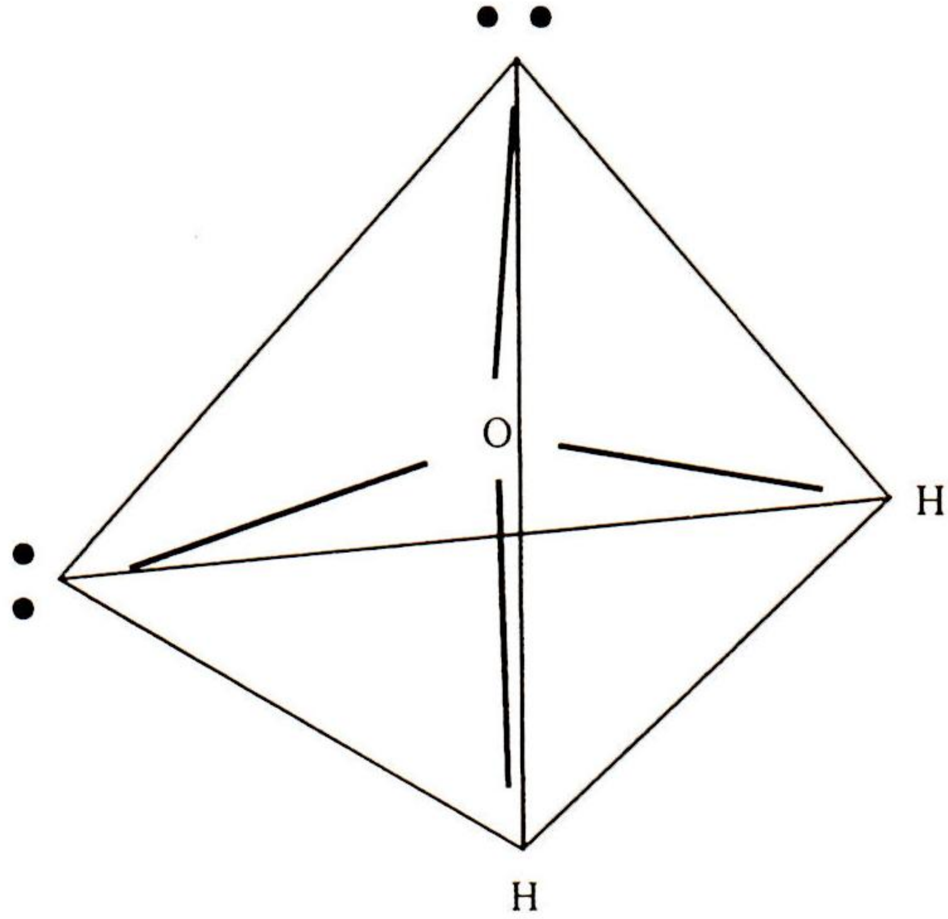


그림 1-23 H_2O 분자에서의 전자 배치.

Quantum mechanical approach

- For a electron in 1-dim. infinite potential box
- Ep = 0 inside the box

The schrodinger equation

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m_e}{h^2} E \psi = 0 \qquad (1\text{-}66)$$

The eigenfunction of schrodinger equation

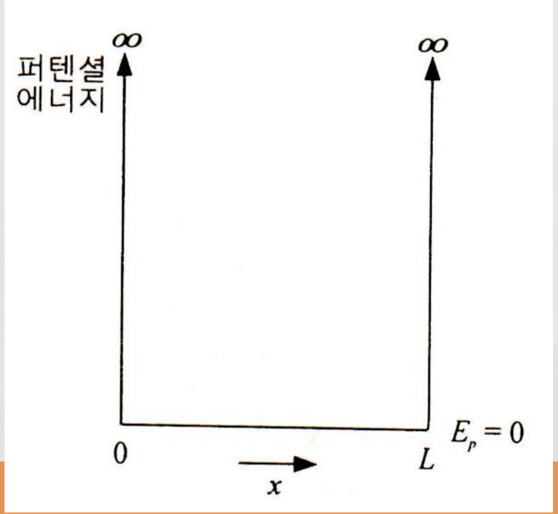
$$\psi(x) = \sin 2\pi k_n x \qquad (1\text{-}67)$$

$$k_n = \frac{n}{2L} \qquad (1\text{-}68)$$

If we substitute the eigenfunction in the eq. (1-66)

$$-(2\pi k_n)^2 \ \psi_n + \frac{8\pi^2 m_e}{h^2} E_n \psi_n = 0 \qquad (1\text{-}69)$$

$$\left\{ -4\pi^2 \left(\frac{n}{2L}\right)^2 + \frac{8\pi^2 m_e}{h^2} E_n \right\} \psi_n = 0 \qquad (1\text{-}70)$$



- The energy eigenvalues are

$$E_n = n^2 \frac{h^2}{8m_e L^2} \qquad (n = 1, 2, 3, \cdots) \qquad (1\text{-}71)$$

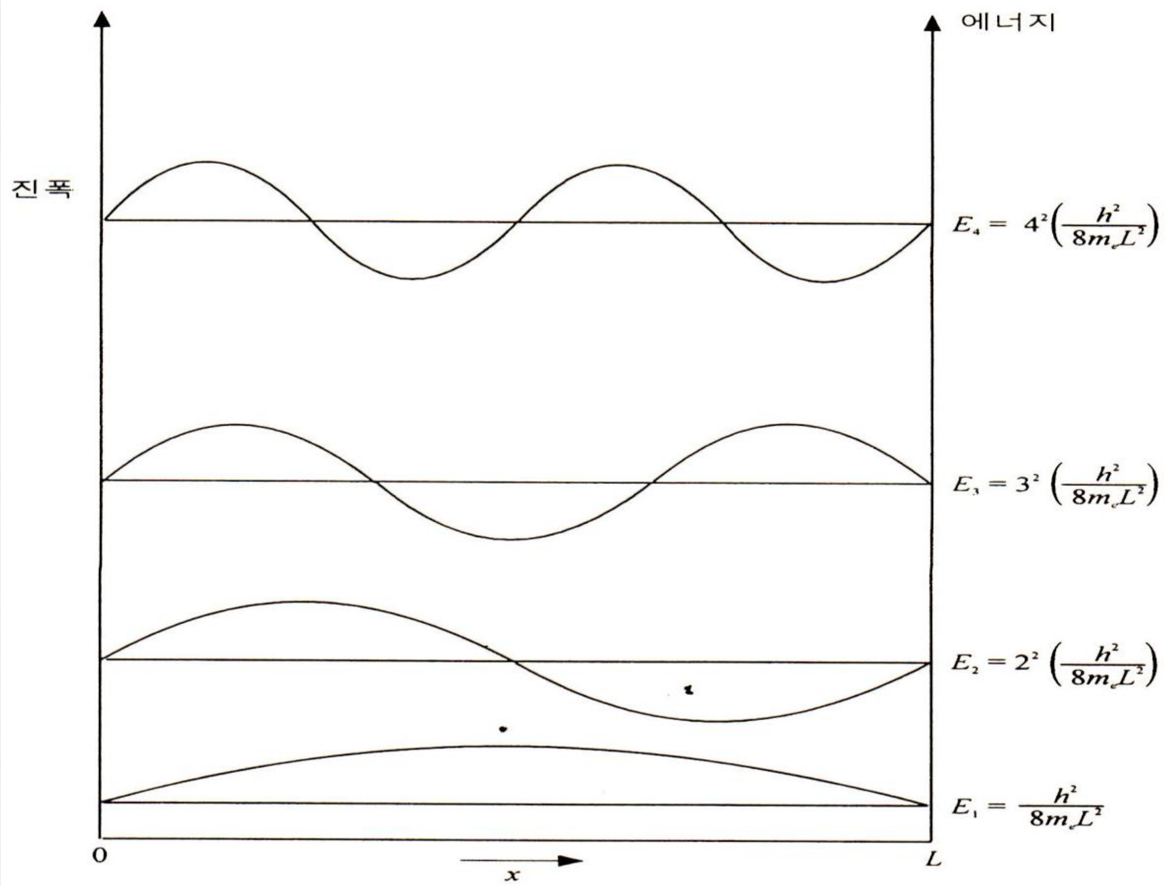


그림 1-25 슈뢰딩거 해에서 나온 첫 네 개의 해와 해당 에너지 값.

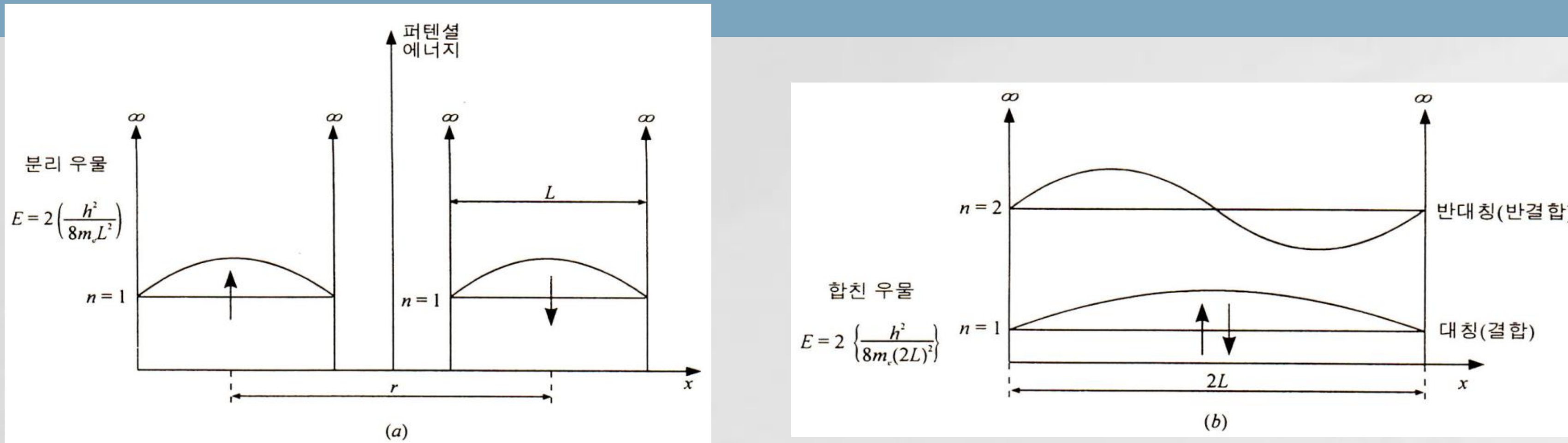


그림 1-26 폭이 L 이면서 분리되어 있는 두 우물(위)와 폭이 $2L$ 로 합쳐져 있는 우물(아래).

$$\psi_r = \begin{cases} \sin 2\pi k_n \left(\frac{r}{2} + \frac{L}{2} - x\right) & \text{오른쪽 우물} \\ 0 & \text{나머지} \end{cases} \tag{1-72}$$

$$\psi_l = \begin{cases} \sin 2\pi k_n \left(\frac{r}{2} + \frac{L}{2} + x\right) & \text{왼쪽 우물} \\ 0 & \text{나머지.} \end{cases} \tag{1-73}$$

The total energy of each potential well system

$$E = 1^2 \frac{h^2}{8m_e L^2} \tag{1-74}$$

The total energy of double potential well system

$$E = 2\frac{h^2}{8m_e L^2} \tag{1-75}$$

- If the wells are enough close to each other and the barrier is removed, as shown in Fig. 1-26, the system will be one well with the width 2L.

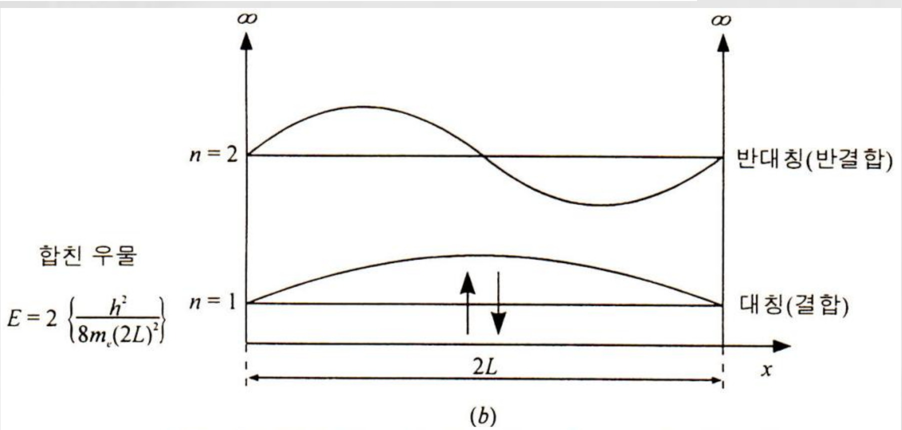
Then, the energy eigenvalue for n=1 state will be

$$E = 1^2 \frac{h^2}{8m_e(2L)^2} \tag{1-76}$$

And, if there are two electrons in that well, the total energy of the system

$$E = 2 \frac{h^2}{8m_e(2L)^2} \tag{1-77}$$

According to the Pauli's exclusion principle, the maximum allowed electron number on the one energy level s "2".



폭이 2L 로 합쳐져 있는 우물(아래).

- By comparing eq. (1-75) and eq. (1-77), on the ground state, the combined well system has ¼ energy of that in the separated well system. That is, if the ground state energy of the double well system is E_0, then that of the single well with twice width will be $E_0/4$.
- Therefore, the total energy of the system will be 75% lower by binding each other.
- The energy diagram of the tsystems has shown in Fig. 1-27.

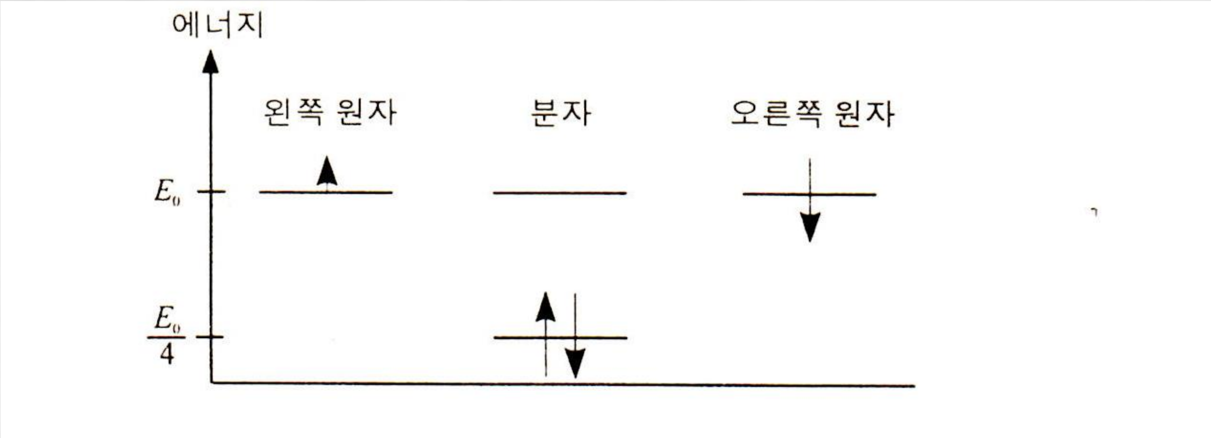


그림 1-27 원자 우물에 있는 전자의 에너지와 분자 우물에 있는 전자의 에너지.

- By the combining of the atoms, 'the bonding molecular orbital' will be established as shown in fig. 1-26(b).
- For n=1 state, the wavefunction is symmetric molecular orbital function, but for n=2 state, the wavefunction is antisymmetric molecular orbital function

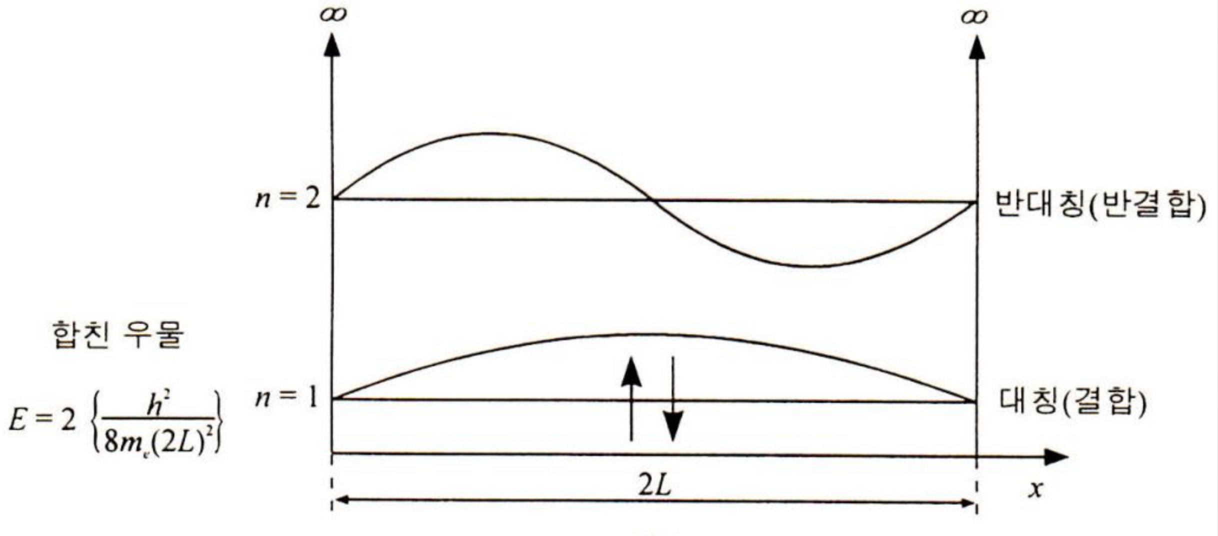


Fig. 1-26(b) 폭이 $2L$ 로 합쳐져 있는 우물(아래).

- Consequently, when two atoms combined, the electrons of each atom make the new molecular orbital for the ground state of molecule.
- Fig. 1-28 shows the analogy between the energy levels of interacting atoms and that of the combined pendulum.

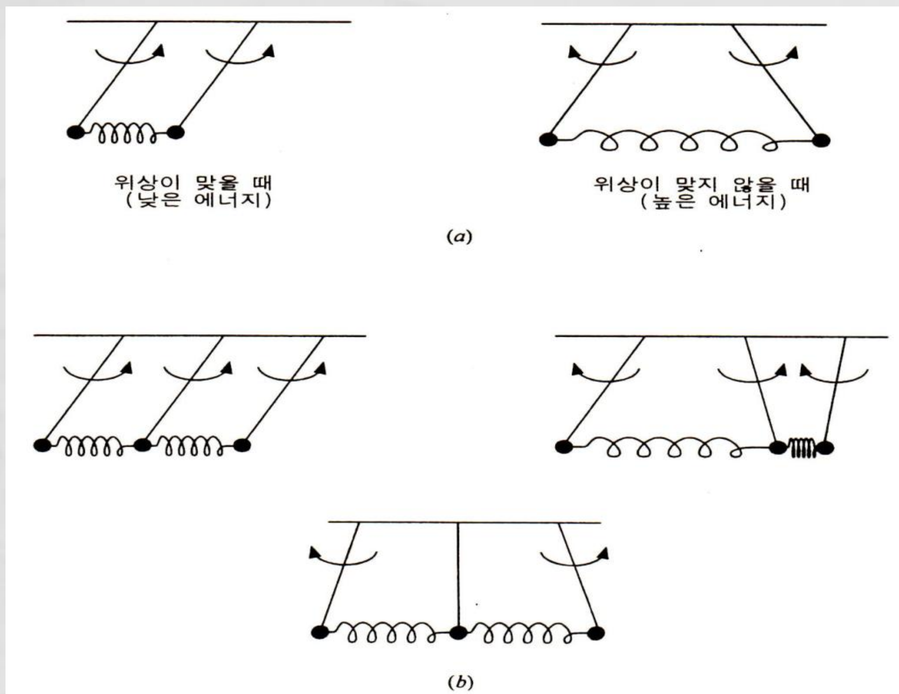


그림 1-28 (a) 2 개의 추와 2 개의 강한 상호 작용을 하는 바닥 상태 전자 파동 함수와의 유사성을 나타내는 그림, (b) 상호 작용하는 파동 함수와 묶여져 있는 추가 3 개로 되었을 때의 그림. 이 때에는 3 개의 에너지 준위가 만들어진다.