Crystal bonding

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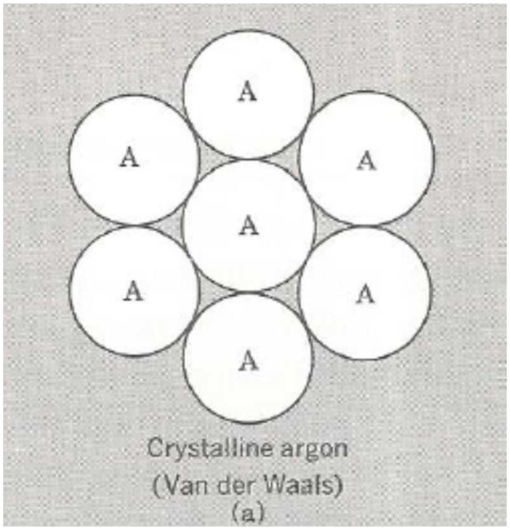
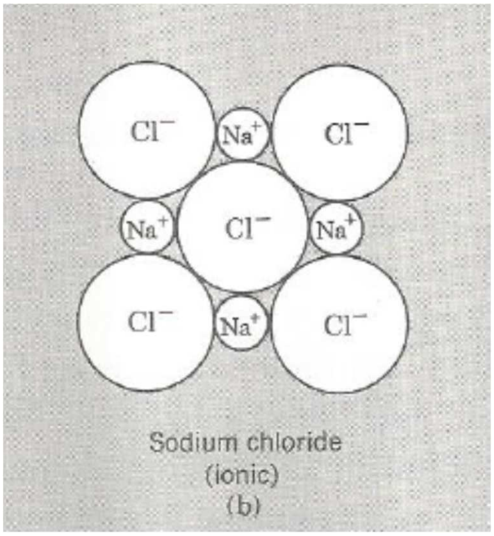
What holds a crystal together? The attractive interaction between the negative charges of the electrobns and the positive charges of the nuclei is responsible for the cohesion of solids. Here we discuss the following topics;

- Covalent bonding
- Hydrogen molecules, hydrogen molecule ion
- Ionic bonding
- Metallic bonding
- Van der Waals interaction (weak interaction)
- Hydrogen bonding

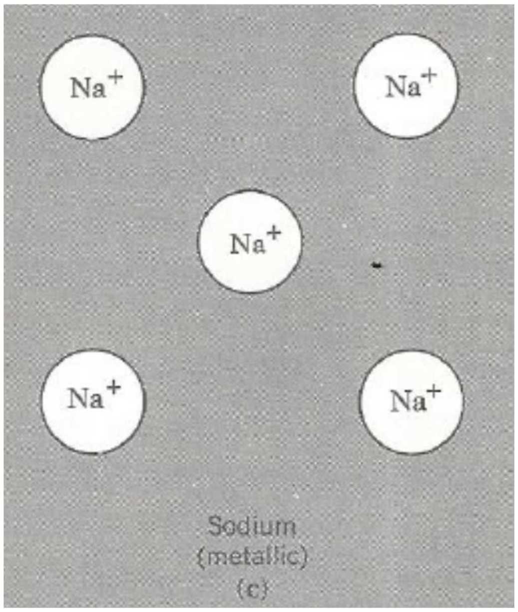
The difference between the mechanism of the bonding are caused mainly by the difference in the distribution of the outermost electrons and the ion cores.

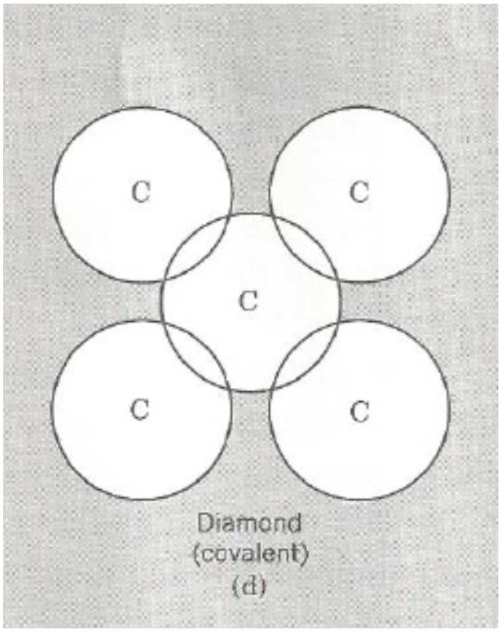


Van der Waals interaction for inert gas



Ionic bonding for NaCl





Metallic Na

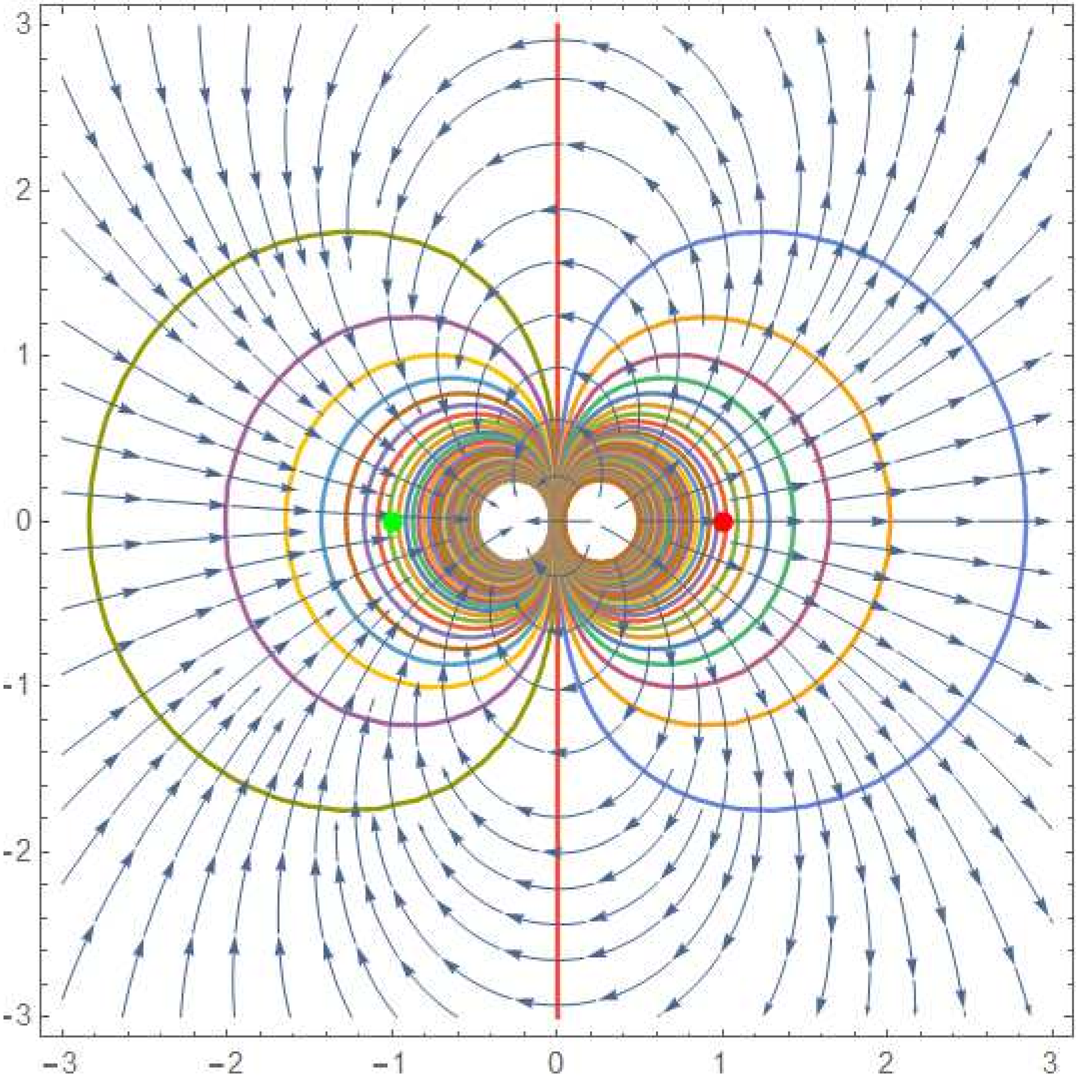
Covalent bonding for diamond

1. van der Waals interaction for inert gas

Electric potential and the electric field distribution

$$V = \frac{e}{r_+} - \frac{e}{r_-},$$

which is the electric potential from a positive charge (+*e*) at $x = d/2$ and a negative charge (-*e*) at $x = -d/2$.



Interaction between electric dipole and electric dipole

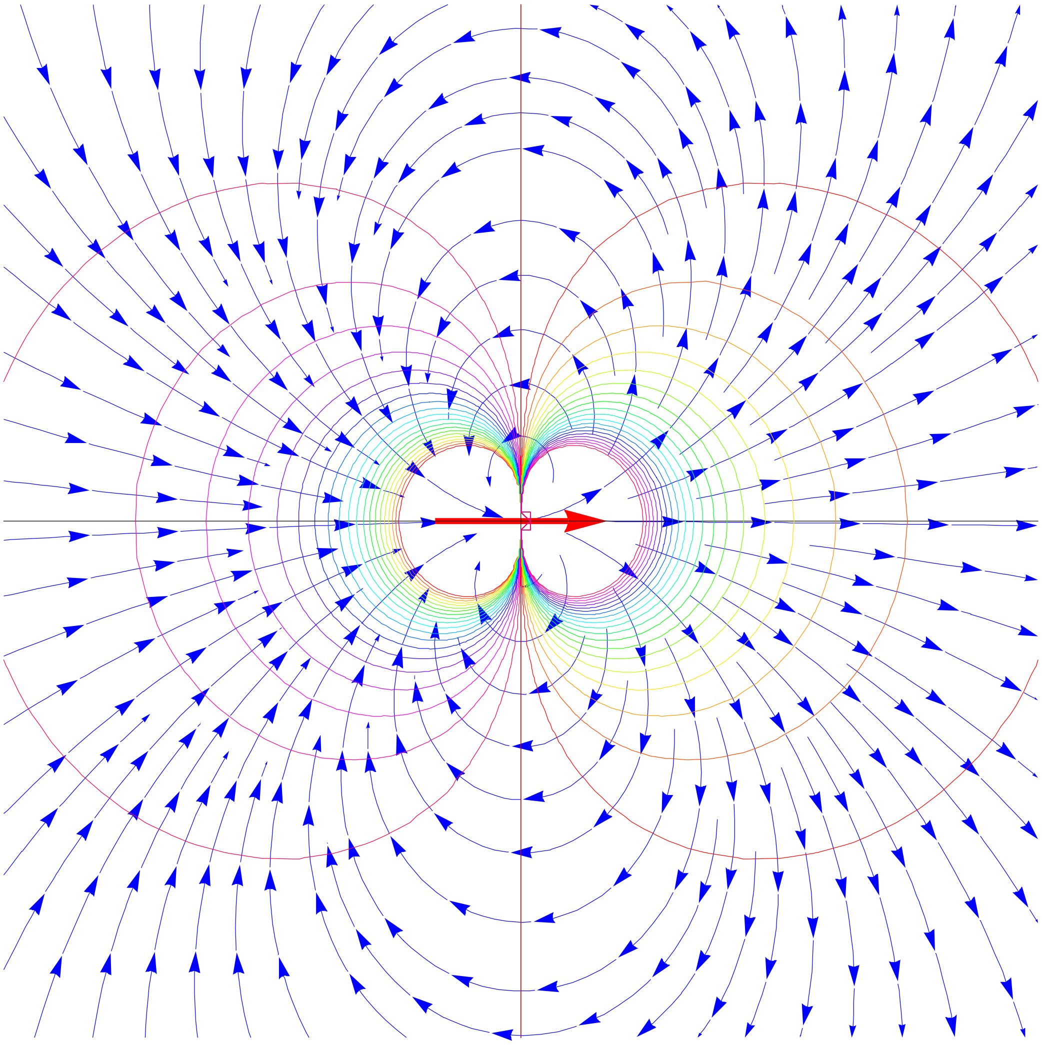


Fig. ContourPlot and StreamPlot of the electric field direction and equi-potential energy from the electric dipole.

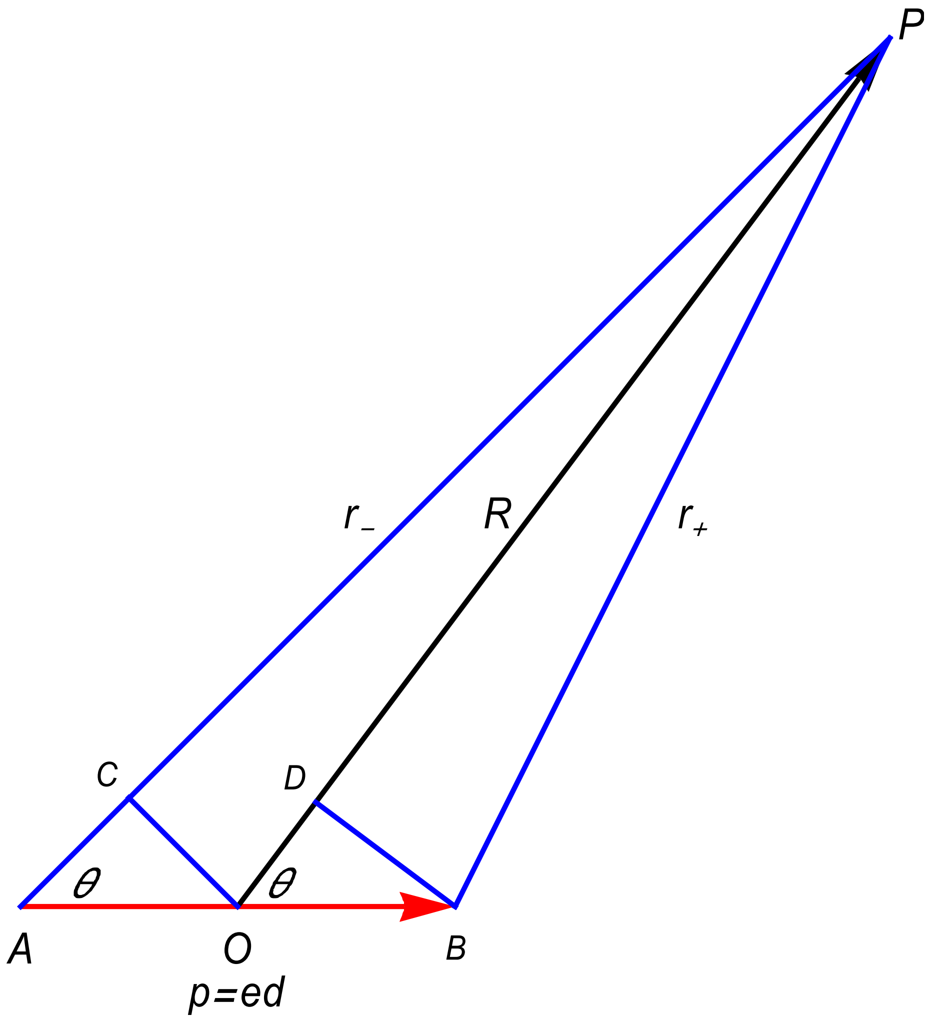


Fig. $p = ed$. $|\overrightarrow{AB}| = d$. $|\overrightarrow{OP}| = R$. $|\overrightarrow{BP}| = |\overrightarrow{DP}| = r_+$. $|\overrightarrow{AP}| = r_-$.

$$r_+ = R - \frac{d}{2}\cos\theta\,, \qquad r_- = R + \frac{d}{2}\cos\theta$$

The electric potential due to the electric dipole ($p = el$) is

$$
\begin{aligned}
\phi &= \frac{e}{r_+} - \frac{e}{r_-} \\
&= e\left(\frac{1}{R - \frac{d}{2}\cos\theta} - \frac{1}{R + \frac{d}{2}\cos\theta}\right) \\
&= \frac{e}{R}\left(\frac{1}{1 - \frac{d}{2R}\cos\theta} - \frac{1}{1 + \frac{d}{2R}\cos\theta}\right) \\
&= \frac{e}{R}[1 + \frac{d}{2R}\cos\theta - (1 - \frac{d}{2R}\cos\theta)] \\
&= \frac{ed}{R^2}\cos\theta
\end{aligned}
$$

or

$$\phi = \frac{p}{R^2}\cos\theta = \frac{\boldsymbol{p}\cdot\boldsymbol{R}}{R^3}$$

The electric field $\boldsymbol{E}$ is given by

$$
\begin{aligned}
\boldsymbol{E} &= -\nabla\phi \\
&= -\boldsymbol{e}_r\frac{\partial\phi}{\partial R} - -\boldsymbol{e}_\theta\frac{1}{R}\frac{\partial\phi}{\partial\theta} \\
&= \boldsymbol{e}_r\frac{2p\cos\theta}{R^2} + \boldsymbol{e}_\theta\frac{p}{R^3}\sin\theta
\end{aligned}
$$

When $\theta = 0$ $\qquad \boldsymbol{E} = \boldsymbol{e}_r\frac{2p}{r^2}$

When $\theta = \frac{\pi}{2}$ $\qquad \boldsymbol{E} = \boldsymbol{e}_\theta\frac{p}{r^2}$

We consider the interaction between the electric dipoles $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$. The electric dipole $\boldsymbol{p}_1$ at the origin leads to the electric potential $\boldsymbol{E}$ for the electric dipole $\boldsymbol{p}_2$ at the position vector $\boldsymbol{R}$, is

$$\boldsymbol{E} = -\nabla\phi$$

where $\qquad \phi = \frac{\boldsymbol{p}_1\cdot R}{R^3}$. The interaction energy between $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ is obtained as

$$U = -\boldsymbol{p}_2 \cdot \boldsymbol{E} = \boldsymbol{p}_2 . \nabla \phi = \boldsymbol{p}_2 . \nabla \left(\frac{\boldsymbol{p}_1 \cdot \boldsymbol{R}}{R^3} \right) \tag{1}$$

or

$$U = \frac{\boldsymbol{p}_1 \cdot \boldsymbol{p}_2}{R^3} - \frac{3(\boldsymbol{p}_1 \cdot \boldsymbol{R})(\boldsymbol{p}_2 \cdot \boldsymbol{R})}{R^5} = -\boldsymbol{p}_2 \cdot [-\frac{\boldsymbol{p}_1}{R^3} + \frac{3(\boldsymbol{p}_1 \cdot \boldsymbol{R})\boldsymbol{R}}{R^5}] \tag{2}$$

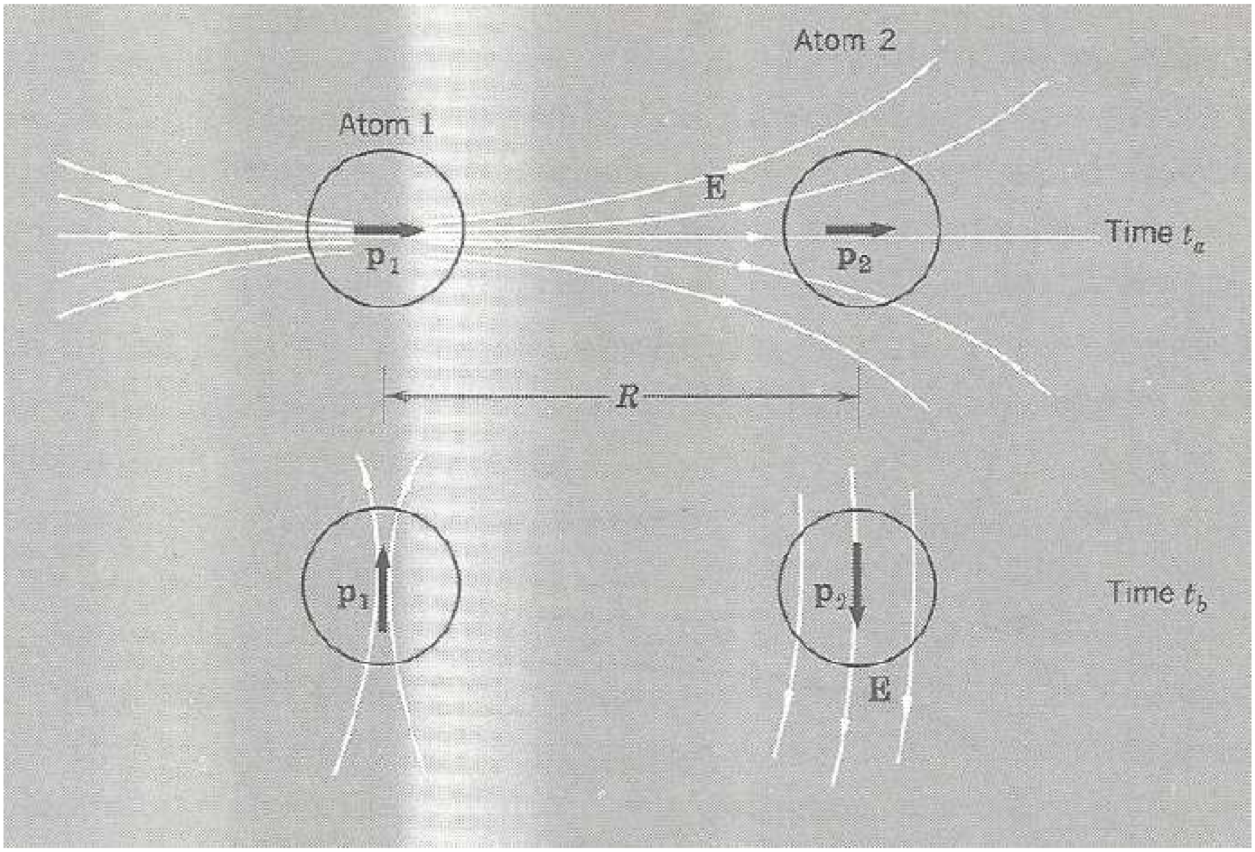
The electric field $\boldsymbol{E}$ is

$$\boldsymbol{E} = -\frac{\boldsymbol{p}_1}{R^3} + \frac{3(\boldsymbol{p}_1 \cdot \boldsymbol{R})\boldsymbol{R}}{R^5}$$

Using the Mathematica, we show the equivalence between Eqs.(1) and (2).

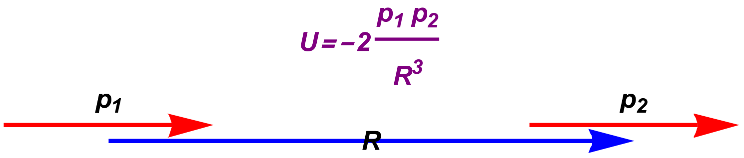
((**Mathematica**))

```
Clear["Gobal`"];
R = Sqrt[x^2 + y^2 + z^2];
r = {x, y, z};
p1 = {p1x, p1y, p1z};
p2 = {p2x, p2y,  p2z};
f1[x_, y_, z_] := p1.r/R^3;
E1 = -Grad[f1[x, y, z], {x, y, z}] // Simplify;
U1 = -p2.E1 // Expand // FullSimplify

U2 = p1.p2/R^3 - 3 (p1.r) (p2.r)/R^5 // FullSimplify;

U1 - U2 // Simplify

0
```

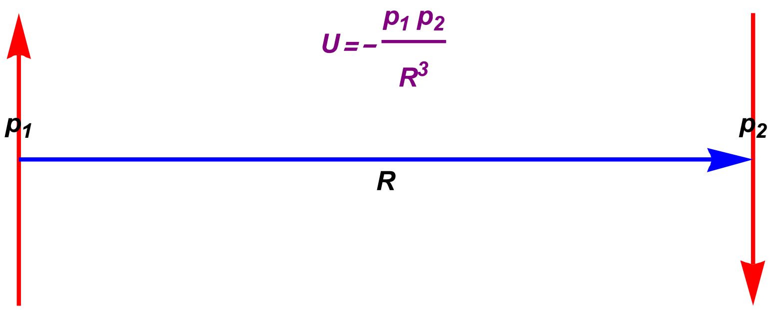


For specified configuration, the interation energy is obtrained as

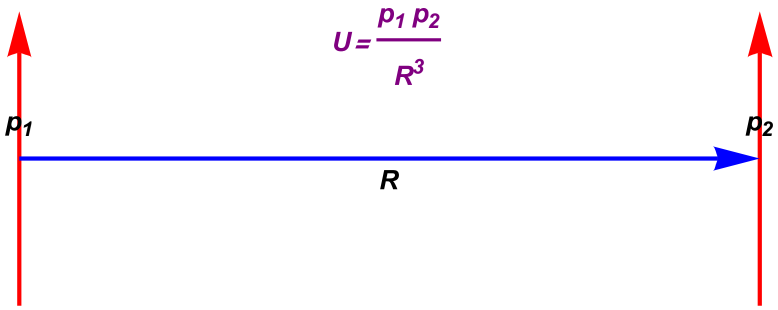
(a)



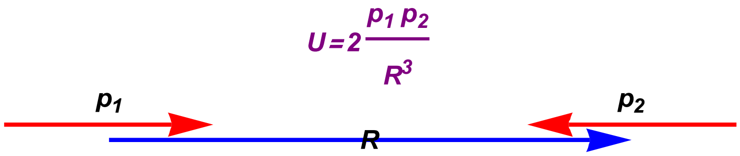
(b)



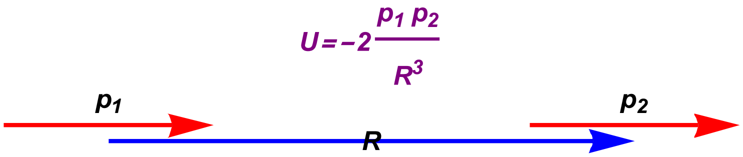
(c)



(d)



2. Van der Waals interaction (attractive)



An electric dipole moment $\boldsymbol{p}_1$ produces an electric field $\boldsymbol{E}$ of magnitude

$$E_2 = \frac{2p_1}{R^3}$$

since

$$U = -2\frac{p_1 p_2}{R^3} = -p_2 E_2$$

This electric field E_2 will induces an instantaneous electric dipole moment p_2 which is given by

$$p_2 = \alpha E_2 = \frac{2\alpha p_1}{R^3}$$

where α is the electric polarizability. Thus we have

$$U = -p_2 E_2 = -\alpha E_2{}^2 = -\frac{4\alpha p_1{}^2}{R^6}$$

The electric polarizability and electric dipole moment are approximated by

$$\alpha \approx r_0{}^3. \qquad p_1 \approx e r_0$$

leading to

$$U = -\frac{4e^2 r_0{}^5}{R^6} = -\frac{C}{R^6}$$

This interaction is called a van der Waals interaction which is attractive.

$$\frac{4e^2 r_0{}^5}{R^6} = 9.22832 \times 10^{-11} \frac{[r_0(A)]^5}{[R(A)]^6} \text{ erg}$$

or

$$\frac{4e^2 r_0{}^5}{R^6} = 57.5986 \frac{[r_0(A)]^5}{[R(A)]^6} \text{ eV}$$

((**Example**)) metallic copper

$$R = 2.55 \text{ Å}, \quad r_0 = 1 \text{ Å}$$

$$\frac{4e^2 r_0{}^5}{R^6} = 3.36 \times 10^{-13} \text{ erg} = 0.21 \text{ eV}$$

3. Electric polarization (quantum mechanics)

((**Polarizability**))

Electric polarizability is the relative tendency of a charge distribution, like the electron cloud of an atom or molecule, to be distorted from its normal shape by an external electric field, which is applied typically by inserting the molecule in a charged parallel-plate capacitor, but may also be caused by the presence of a nearby ion or dipole.

The electronic polarizability α is defined as the ratio of the induced dipole moment *P* of an atom to the electric field *ε* that produces this dipole moment.

$$p = \alpha\varepsilon$$

The work done on the system as *ε* slightly changes to *ε*+d*ε*,

$$dW = -pd\varepsilon = -\alpha\varepsilon d\varepsilon$$

or

$$W = \Delta E = -\frac{1}{2}\alpha\varepsilon^2$$

4. Polarizability of the 1s-state

$$|\psi_{1s}\rangle = |1,0,0\rangle + e\varepsilon\sum_{\substack{n\neq 1\\ l,m}}|n,l,m\rangle\frac{\langle n,l,m|\hat{z}|1,0,0\rangle}{E_1^{(0)} - E_n^{(0)}} + \ldots$$

$$p = \langle\psi_{1s}|(-e\hat{z})|\psi_{1s}\rangle = -2e^2\varepsilon\sum_{\substack{n\neq 1\\ l,m}}\frac{|\langle n,l,m|\hat{z}|1,0,0\rangle|^2}{E_1^{(0)} - E_n^{(0)}} = \alpha\varepsilon$$

or

$$\alpha = -2e^2\sum_{\substack{n\neq 1\\ l,m}}\frac{|\langle n,l,m|\hat{z}|1,0,0\rangle|^2}{E_1^{(0)} - E_n^{(0)}}$$

Under the perturbation, the energy shift is given by

$$\Delta E = e^2\varepsilon^2\sum_{\substack{n\neq 1\\ l,m}}\frac{\langle n,1,m|\hat{z}|1,0,0\rangle^2}{E_1^{(0)} - E_n^{(0)}} = -\frac{\alpha\varepsilon^2}{2}$$

((Note-1))

$$\langle \psi_{1s} |(-e\hat{z})| \psi_{1s} \rangle = (\langle 1,0,0| + e\varepsilon \sum_{\substack{n\neq 1 \\ l,m}} \langle n,l,m| \frac{\langle n,l,m|\hat{z}|1,0,0\rangle^{*}}{(E_1^{(0)} - E_n^{(0)})} + ...)(-e\hat{z})$$

$$\times (|1,0,0\rangle + e\varepsilon \sum_{\substack{n\neq 1 \\ l,m}} |n,l,m\rangle \frac{\langle n,l,m|\hat{z}|1,0,0\rangle}{(E_1^{(0)} - E_n^{(0)})} + ...)$$

The electric field ε causes an induced dipole moment to appear, proportional to ε.

((**Note-2**))

Since

$$\langle 1,0,0|\hat{z}|1,0,0\rangle = 0 \text{ and } E_n^{(0)} - E_1^{(0)} \geq E_2^{(0)} - E_1^{(0)} > 0$$

we have

$$\alpha = 2e^2 \sum_{\substack{n\neq 1 \\ l,m}} \frac{|\langle n,l,m|\hat{z}|1,0,0\rangle|^2}{E_n^{(0)} - E_1^{(0)}} \leq \frac{2e^2}{E_2^{(0)} - E_1^{(0)}} \sum_{\substack{n\neq 1 \\ l,m}} |\langle n,l,m|\hat{z}|1,0,0\rangle|^2$$

$$= \frac{2e^2}{E_2^{(0)} - E_1^{(0)}} \sum_{\substack{n, \\ l,m}} |\langle n,l,m|\hat{z}|1,0,0\rangle|^2$$

Here

$$\sum_{\substack{n, \\ l,m}} |\langle n,l,m|\hat{z}|1,0,0\rangle|^2 = \sum_{\substack{n, \\ l,m}} \langle 1,0,0|\hat{z}|n,l,m\rangle\langle n,l,m|\hat{z}|1,0,0\rangle = \langle 1,0,0|\hat{z}^2|1,0,0\rangle$$

Then we have

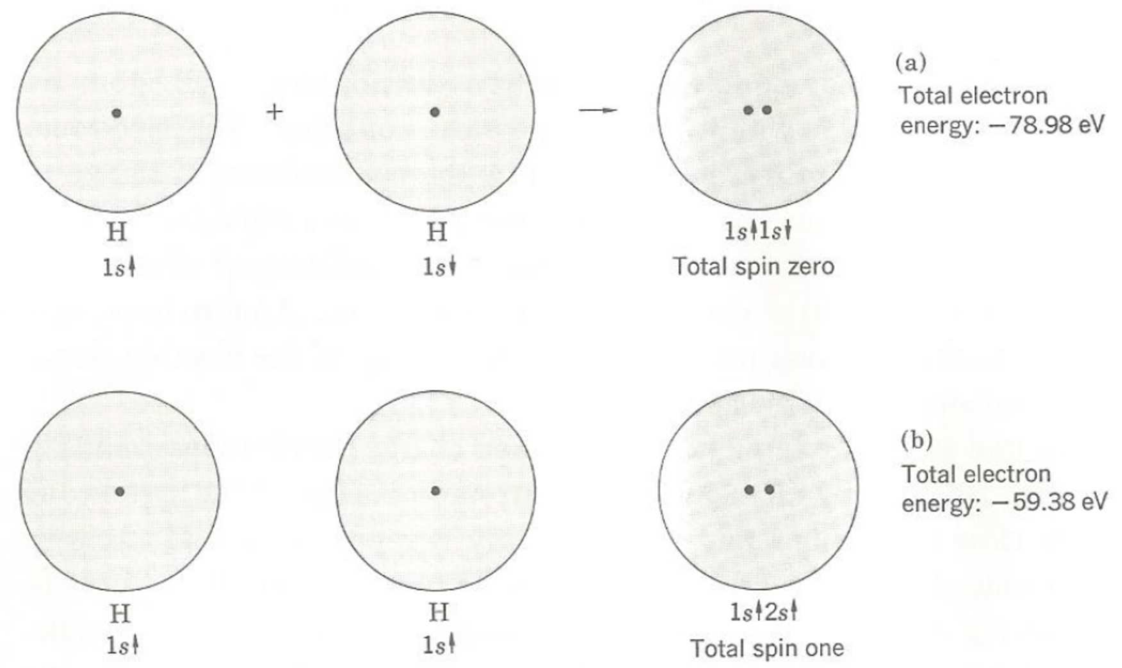
$$\alpha \leq \frac{2e^2}{E_2^{(0)} - E_1^{(0)}} \sum_{\substack{n, \\ l,m}} |\langle n,l,m|\hat{z}|1,0,0\rangle|^2 = \frac{2e^2}{E_2^{(0)} - E_1^{(0)}} \langle 1,0,0|\hat{z}^2|1,0,0\rangle$$

$$\alpha \leq \frac{2e^2}{\frac{e^2}{2a_0}(1-\frac{1}{4})} a_0^{\ 2} = \frac{16}{3} a_0^{\ 3} = 5.33 a_0^{\ 3}$$

which is consistent with the experimentally observed value: $\alpha = 4.5\, a_0^3$.

$$\langle 1,0,0|\hat{z}^2|1,0,0\rangle = a_0^{\,2}$$

5. Repulsive interaction (the inert gas)



The Pauli exclusion principle prevents two electrons from occupying the same quantum state:. The electron distributions of atoms with closed shells can overlap only if accompanied by the partial promotion of electrons to unoccupied higher energy states of the atoms. Thus the electron overlap increases the total energy of the system, giving a repulsive contribution to the interaction. An extreme example in which the overlap is complete is shown in the above figure (Kittel, ISSP, 4-th edition).

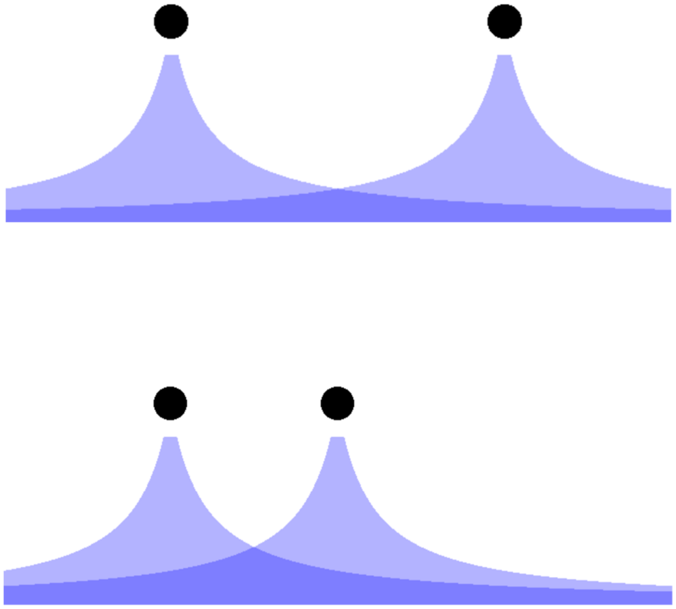


Fig. Electronic charge distributions overlap as atoms approach. The solid circles denote the nuclei (the origin of the repulsive interaction, due to the Pauli's exclusion principle).

6. Lennard-Jones interaction

The Lennard-Jones interaction consist of the attractive potential (van der Waals weak interaction) and the repulsive interaction;

$$U(R) = 4\varepsilon[(\frac{\sigma}{R})^{12} - (\frac{\sigma}{R})^{6}]$$

From $\frac{dU(R)}{dR} = 0$, $U(R)$ has a local minimum $-\varepsilon$ at $\frac{R}{\sigma} = 2^{1/6}$=1.12246.

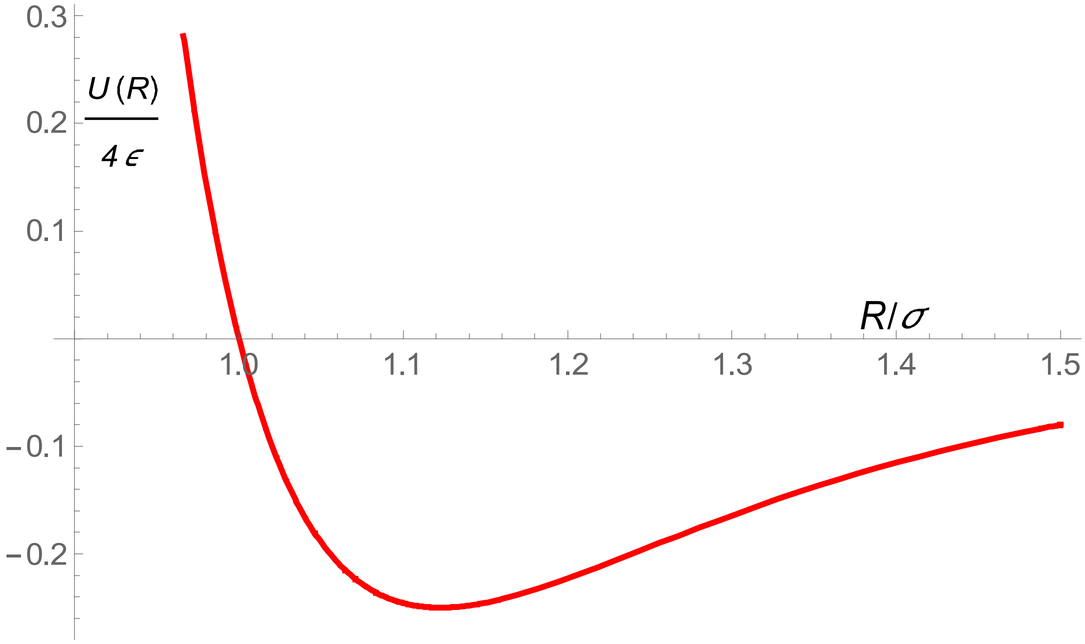


Fig. Lennard-Jones potential. The value of U at the minimum is $-\varepsilon$ at $R = 1.12246\sigma$.

7. Ionic crystal: NaCl

In ionic bonding, electrons are transferred from one atom to another resulting in the formation of positive and negative ions. The electrostatic attractions between the positive and negative ions hold the compound together.

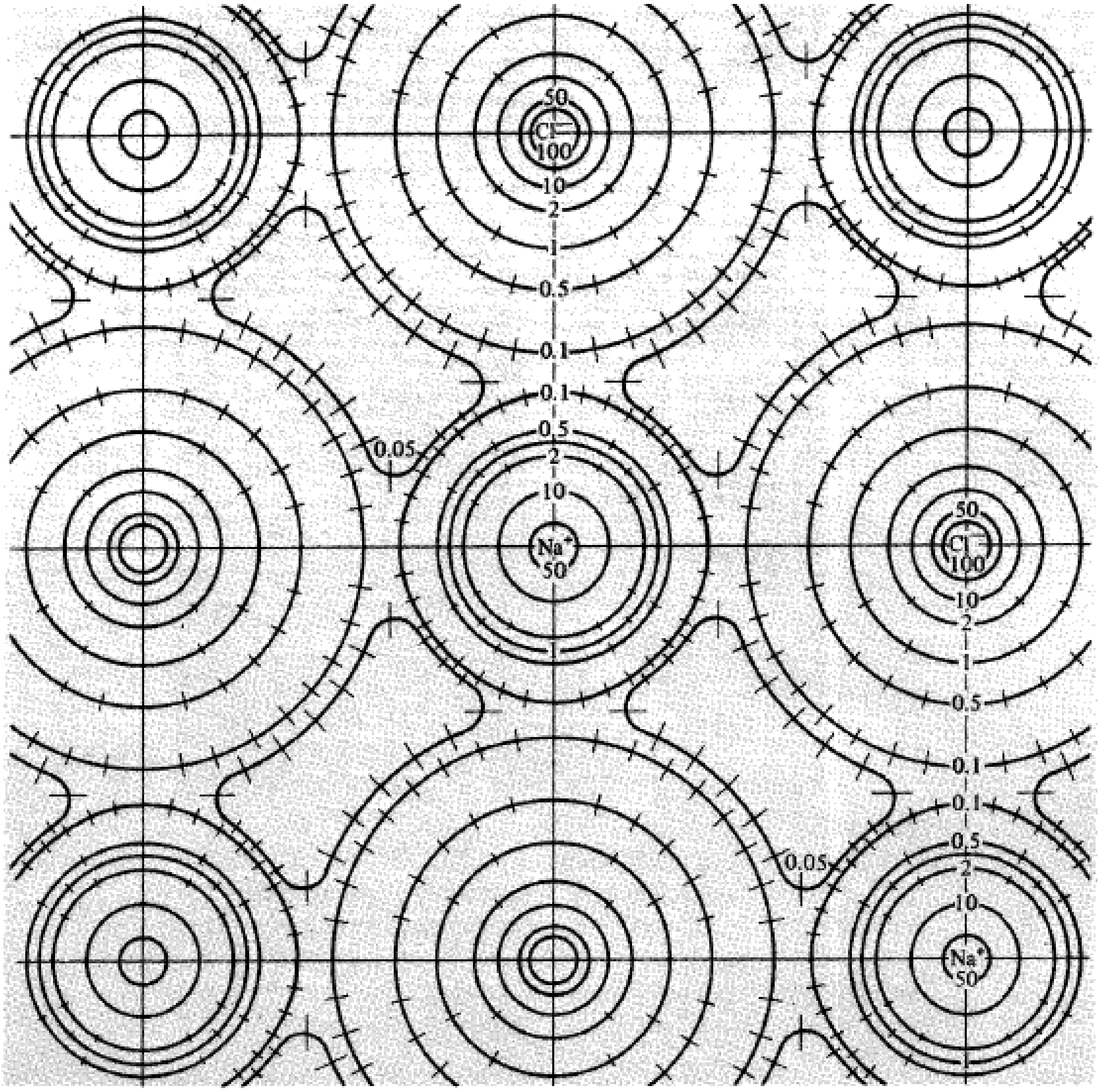


Fig. Electron density distribution in the base plane of NaCl, after x-ray studies (C. Kittel, ISSP 4-th edition).

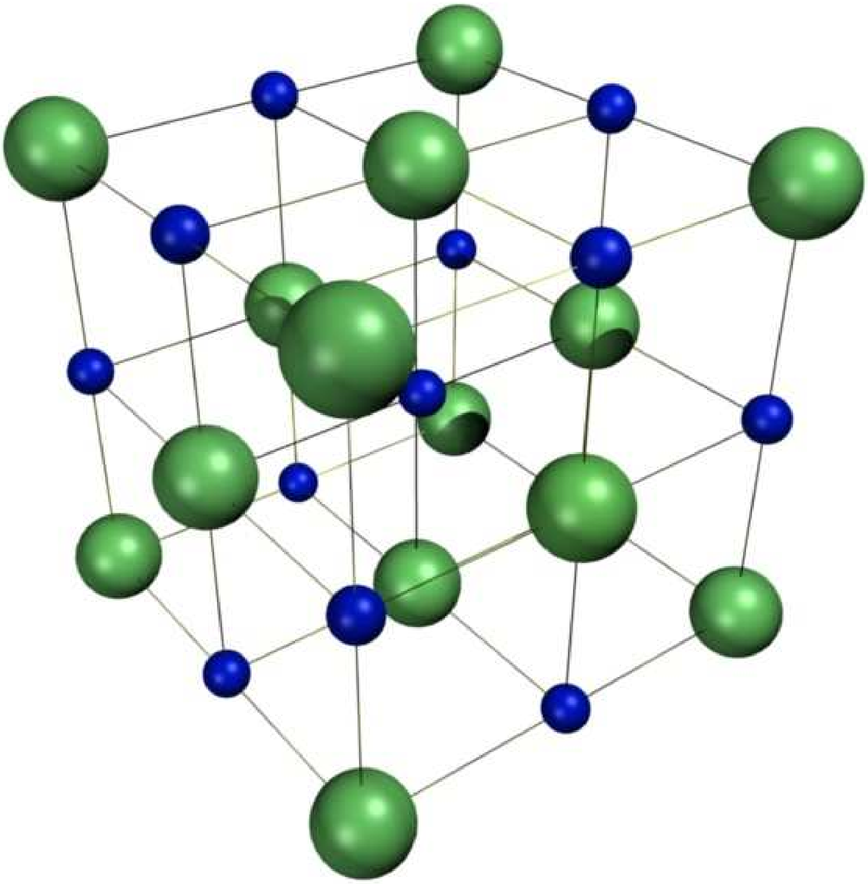


Fig. Crystal structure of NaCl. The lattice constant of the conventional cubic cell is a = 5.6402 Å

In the ionic crystal (typically NaCl), the van der Waals part of the attractive interaction in ionic crystal can be neglected. The potential energy can be expressed by

$$U = N(z\lambda e^{-R/\rho} - \frac{\alpha e^2}{R}),$$

where z is the number of the nearest neighbors of any ion and α is the Madelung constant. For NaCl, α is given by

$$\alpha = 1.747565.$$

Note that the interaction between the nearest neighbor ions is given by

$$\lambda e^{-R/\rho} - \frac{e^2}{R}.$$

The first term is repulsive interaction, while the second term is attractive interaction. From the condition that $dU/dR = 0$ at $R = R_0$, we have

$$R_0^{\ 2} \exp(-\frac{R_0}{\rho}) = \frac{\rho\alpha e^2}{z\lambda}.$$

The minimum value of U at $R = R_0$ is

$$U(R_0) = \frac{Ne^2\alpha(R_0 - \rho)}{R_0^{\ 2}}.$$

((**Example**)) NaCl

$\rho = 0.321$ Å, $z\lambda$= 1. 05 Å, $\alpha =$ 1.747565. cal=4.184 J.

Using these values, we get R_0 = 2.81463 Å

$U(R_0)$ = -182.53 kcal/mol= -763.70 kJ/mol

$$\frac{U(R_0)}{N} = \text{-7.92091 eV}.$$

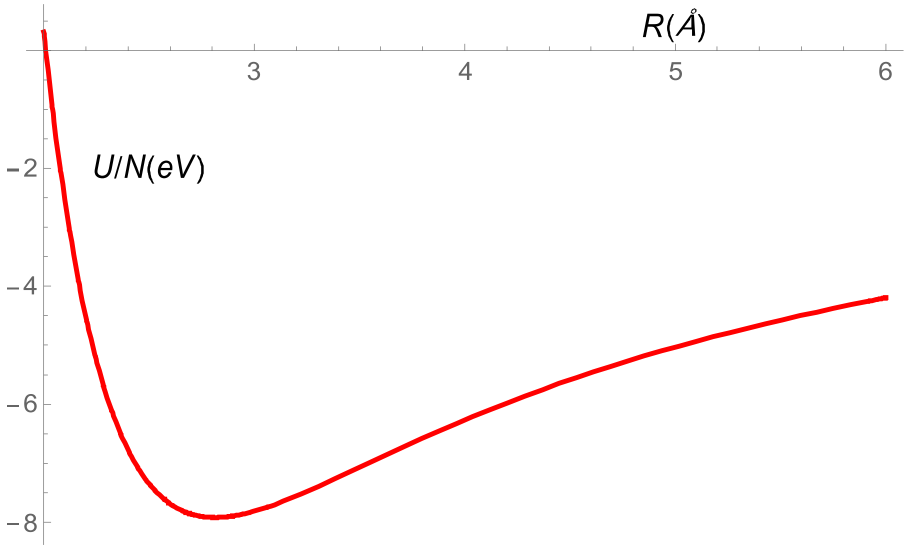


Fig. Energy per molecule of NaCl crystal. The minimum of U/N is -7.92091 eV at R = 2.81463 Å.

((**Note**)) Calculation of Madelung constant a (see the Appendix). We use the Evjen's method.

$\alpha =$ 1.747565. for NaCl

8. Hydrogen molecule H_2^+: covalent bonding

(a) Definition of H_2^+

The hydrogen molecular ion, or H_2^+, is the simplest molecular ion. It is composed of two positively charged protons and one negatively charged electron, and can be formed from ionization of a neutral hydrogen molecule. It is of great historical and theoretical interest because, having only one electron, the Schrödinger equation for the system can be solved in a relatively straightforward way due to the lack of electron–electron repulsion (electron correlation).

We now consider the hydrogen molecule formed of one electron and two protons, where these two protons are widely separated. What is the lowest energy of this system? There are two possible states.

(i) The electron is close to one of the proton, forming a hydrogen atom in the ground state. (ii) The electron is close to the other proton, forming a hydrogen atom in the ground state.

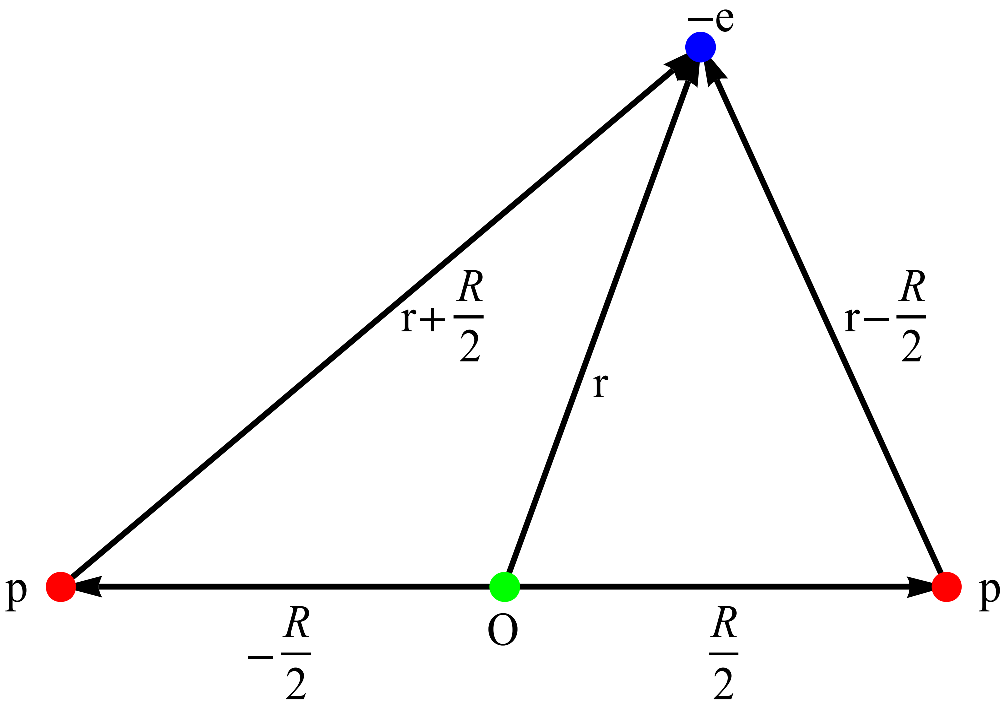


Fig. The co-ordinates of the two protons and one electron used in the discussion of hydrogen molecule ion. R is the distance between two protons.

(i) When R becomes very large and the electron is close to one of the proton, the total energy of the electron is close to the energy of the hydrogen atom.

$$E_0 = -13.6 \text{ eV}.$$

(ii) When R becomes very small, the total energy of the electron is close to the energy of the He atom (system of the two protons and one electron),

$$E_0 = -54.4 \text{ eV}.$$

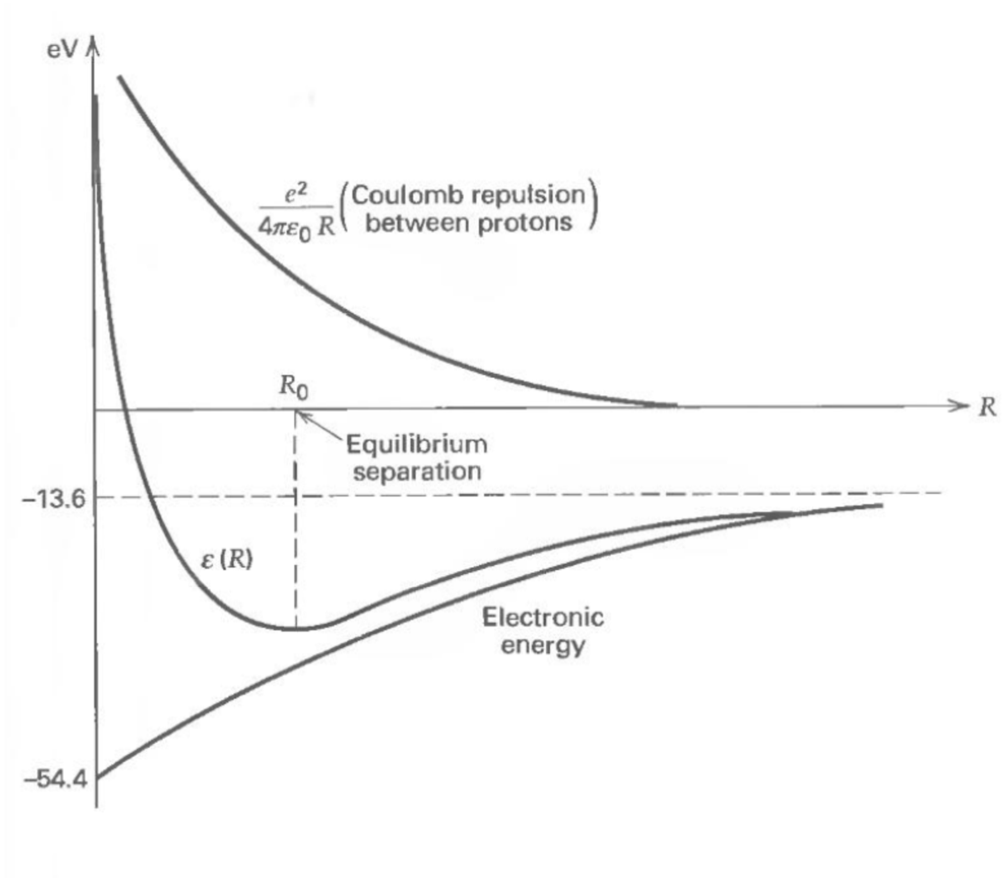


Fig. Rough prediction of E_0 vs R. R increases with increasing R from -54.4 eV at R = 0 [He atom (system of the two protons and one electron)) to -13.6 eV at $R = \infty$ (hydrogen atom)

(b) Wave function and Hamiltonian

We consider the wave function of the system of one electron and two protons.
The wave function of electron is given by

$$\psi_{1s}(\boldsymbol{r}_1) = \langle \boldsymbol{r}_1 | 1s \rangle = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-\frac{|\boldsymbol{r}_1|}{a_0}} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-\frac{1}{a_0}\left|\boldsymbol{r}-\frac{1}{2}\boldsymbol{R}\right|} = \langle \boldsymbol{r}_1 | \psi_1 \rangle$$

$$\psi_{1s}(\boldsymbol{r}_2) = \langle \boldsymbol{r}_2 | 1s \rangle = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-\frac{|\boldsymbol{r}_2|}{a_0}} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-\frac{1}{a_0} e^{-\frac{1}{a_0}\left|\boldsymbol{r}+\frac{1}{2}\boldsymbol{R}\right|}} = \langle \boldsymbol{r}_2 | \psi_2 \rangle$$

where a_0 (=0.53 Å) is a Bohr radius,

$$E_{1s} = -\frac{e^2}{2a_0} = -R = \text{-13.6 eV}$$

and

$$\boldsymbol{r}_1 = \boldsymbol{r} - \frac{1}{2}\boldsymbol{R}, \qquad \boldsymbol{r}_2 = \boldsymbol{r} + \frac{1}{2}\boldsymbol{R}.$$

The Hamiltonian of the system is given by

$$\hat{H} = \frac{\hat{\boldsymbol{p}}^2}{2m_e} - \frac{e^2}{\left|\hat{\boldsymbol{r}} - \frac{\boldsymbol{R}}{2}\right|} - \frac{e^2}{\left|\hat{\boldsymbol{r}} + \frac{\boldsymbol{R}}{2}\right|} + \frac{e^2}{|\boldsymbol{R}|}.$$

We have the commutation relation for the parity operator as

$$\hat{\pi}\hat{H}\hat{\pi} = \hat{H}, \qquad \text{or} \qquad [\hat{\pi}, \hat{H}] = 0$$

since

$$\hat{\pi}\hat{\boldsymbol{p}}\hat{\pi}^+ = -\hat{\boldsymbol{p}}, \qquad \hat{\pi}\hat{\boldsymbol{r}}\hat{\pi}^+ = -\hat{\boldsymbol{r}}, \qquad \hat{\pi} = \hat{\pi}^+ = \hat{\pi}^{-1}.$$

(c) Properties of the kets $|\psi_1\rangle$ and $|\psi_2\rangle$

A positively ionized hydrogen molecule consists of two protons with one electron worming its way around them. If two protons are very far apart, the electron will stay close to one proton and form a hydrogen atom in its lowest state, and the other proton will remain alone as a positive ion. If the two protons are far apart, we can visualize one physical state in which the electron is attached to one of protons. There is another state symmetric to the one, in which the electron is near the other proton, and the first proton is the one that is an ion. We will take these two states as our basis states, and we call these $|\psi_1\rangle$ and $|\psi_2\rangle$.

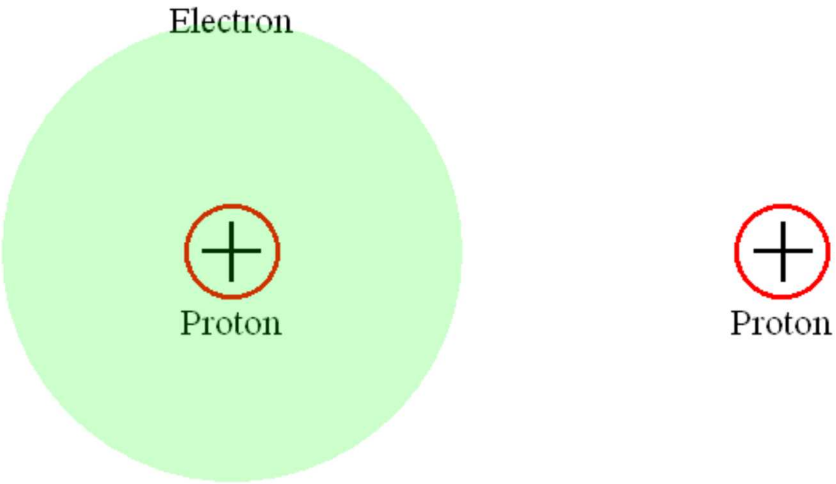


Fig. The state $|\psi_1\rangle$ for the two protons and one electron.

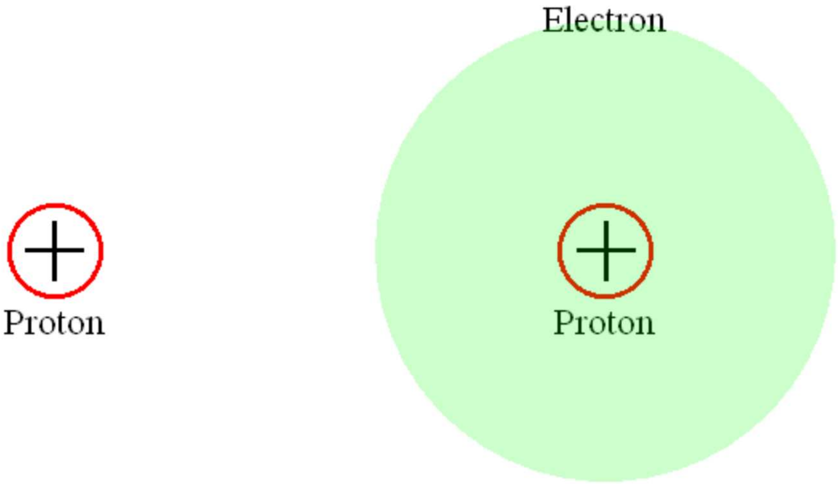


Fig. The state $|\psi_2\rangle$ for the two protons and one electron

$|\psi_1\rangle$ and $|\psi_2\rangle$ are the eigenkets such that

$$\left(\frac{\hat{\boldsymbol{p}}^2}{2m_e} - \frac{e^2}{\left|\hat{\boldsymbol{r}} - \frac{\boldsymbol{R}}{2}\right|}\right)|\psi_1\rangle = E_{1s}|\psi_1\rangle$$

$$(\frac{\hat{\boldsymbol{p}}^2}{2m_e}-\frac{e^2}{\left|\hat{\boldsymbol{r}}+\frac{\boldsymbol{R}}{2}\right|})\left|\psi_2\right\rangle = E_{1s}\left|\psi_2\right\rangle$$

Note that $\langle \boldsymbol{r}|\psi_1\rangle = \psi_1(\boldsymbol{r})$ is the wave function of the hydrogen atom when only proton 1 exists. $\langle \boldsymbol{r}|\psi_2\rangle = \psi_2(\boldsymbol{r})$ is the wave function of the hydrogen atom when only proton 2 exists. In practice, proton 1 or proton 2 does not exist alone, but the two protons exist with a finite separation. Even them if their separation is very large, we can consider either $\psi_1(\boldsymbol{r})$ or $\psi_2(\boldsymbol{r})$ as the eigenfunction of the whole system in a zeroth order approximation. Thus the state of this system is doubly degenerate in this approximation.

We have the relation such that

$$\hat{\pi}\hat{H}_1\hat{\pi} = \hat{H}_2, \qquad \hat{\pi}\hat{H}_2\hat{\pi} = \hat{H}_1$$

or

$$\hat{\pi}\hat{H}_1 = \hat{H}_2\hat{\pi}, \qquad \hat{\pi}\hat{H}_2 = \hat{H}_1\hat{\pi}$$

where

$$\hat{H}_1 = \frac{\hat{\boldsymbol{p}}^2}{2m_e}-\frac{e^2}{\left|\hat{\boldsymbol{r}}-\frac{\boldsymbol{R}}{2}\right|}, \qquad \hat{H}_2 = \frac{\hat{\boldsymbol{p}}^2}{2m_e}-\frac{e^2}{\left|\hat{\boldsymbol{r}}+\frac{\boldsymbol{R}}{2}\right|}$$

Suppose that $\left|\psi_1\right\rangle$ is the eigenket of $\hat{H}_1$ with the eigenvalue E_{1s};

$$\hat{H}_1\left|\psi_1\right\rangle = E_{1s}\left|\psi_1\right\rangle$$

$\left|\psi_2\right\rangle$ is the eigenket of $\hat{H}_2$ with the same eigenvalue E_{1s};

$$\hat{H}_2\left|\psi_2\right\rangle = E_{1s}\left|\psi_2\right\rangle$$

In the $\left|\boldsymbol{r}\right\rangle$ representation, we have

$$\langle \boldsymbol{r}|\hat{H}_1|\psi_1\rangle = E_{1s}\langle \boldsymbol{r}|\psi_1\rangle, \qquad \langle \boldsymbol{r}|\hat{H}_2|\psi_2\rangle = E_{1s}\langle \boldsymbol{r}|\psi_2\rangle$$

or

$$(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{\left|\boldsymbol{r}-\frac{\boldsymbol{R}}{2}\right|})\psi_1(\boldsymbol{r}) = E_{1s}\psi_1(\boldsymbol{r}) \qquad (1)$$

$$(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{\left|\boldsymbol{r}+\frac{\boldsymbol{R}}{2}\right|})\psi_2(\boldsymbol{r}) = E_{1s}\psi_2(\boldsymbol{r}) \qquad (2)$$

When the replacement ($\boldsymbol{r} \rightarrow -\boldsymbol{r}$) is made in Eq.(1), Eq,(1) is changed into

$$(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{\left|\boldsymbol{r}+\frac{\boldsymbol{R}}{2}\right|})\psi_1(-\boldsymbol{r}) = E_{1s}\psi_1(-\boldsymbol{r}) \qquad (3)$$

The comparison between Eqs.(2) and (3) leads to the relation

$$\psi_1(-\boldsymbol{r}) = \psi_2(\boldsymbol{r})$$

or

$$\langle -\boldsymbol{r}|\psi_1\rangle = \langle \boldsymbol{r}|\psi_2\rangle$$

or

$$\langle \boldsymbol{r}|\hat{\pi}|\psi_1\rangle = \langle \boldsymbol{r}|\psi_2\rangle$$

where we use the parity operator; $\hat{\pi}|\boldsymbol{r}\rangle = |-\boldsymbol{r}\rangle$ and $\langle \boldsymbol{r}|\hat{\pi} = \langle -\boldsymbol{r}|$. So that we get the final result

$$\hat{\pi}|\psi_1\rangle = |\psi_2\rangle, \qquad \text{or} \qquad \hat{\pi}|\psi_2\rangle = \hat{\pi}^2|\psi_1\rangle = |\psi_1\rangle$$

Note that

$$\langle \boldsymbol{r}|\hat{\pi}|\psi_1\rangle = \langle -\boldsymbol{r}|\psi_1\rangle = \langle \boldsymbol{r}|\psi_2\rangle, \qquad \text{or} \qquad \psi_1(-\boldsymbol{r}) = \psi_2(\boldsymbol{r})$$

$$\langle \boldsymbol{r}|\hat{\pi}|\psi_2\rangle = \langle -\boldsymbol{r}|\psi_2\rangle = \langle \boldsymbol{r}|\psi_1\rangle, \text{ or} \qquad \text{or} \qquad \psi_2(-\boldsymbol{r}) = \psi_1(\boldsymbol{r})$$

(d) Even function and odd function

Since $[\hat{\pi}, \hat{H}] = 0$, there is a simultaneous eigenket of $\hat{H}$ and $\hat{\pi}$.

$$\hat{H}|\psi\rangle = E|\psi\rangle, \qquad \hat{\pi}|\psi\rangle = \lambda|\psi\rangle$$

We use the relation

$$\hat{\pi}|\psi_1\rangle = |\psi_2\rangle, \qquad \hat{\pi}|\psi_2\rangle = |\psi_1\rangle$$

The matrix of $\hat{\pi}$ under the basis of $\{|\psi_1\rangle, |\psi_2\rangle\}$ is given by

$$\hat{\pi} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \hat{\sigma}_x$$

The eigenkets of $\hat{\pi}$ is as follows.

(i) Even parity (the gerade (even) state); eigenvalue (+1)

$$|\psi_e\rangle = C_e(|\psi_1\rangle + |\psi_2\rangle),$$

or

$$\psi_e(\boldsymbol{r}) = \langle \boldsymbol{r}|\psi_e\rangle = C_e[\psi_1(\boldsymbol{r}) + \psi_2(\boldsymbol{r})]$$

(ii) Odd parity (the ungerade (odd) state); eigenvalue (-1)

$$|\psi_o\rangle = C_o(|\psi_1\rangle - |\psi_2\rangle)$$

or

$$\psi_o(\boldsymbol{r}) = \langle \boldsymbol{r}|\psi_o\rangle = C_o[\psi_1(\boldsymbol{r}) - \psi_2(\boldsymbol{r})]$$

Note that constants C_e and C_o can be determined from the normalization condition later.

(e) Correlation function $S(\boldsymbol{R}) = \langle \psi_1 | \psi_2 \rangle$

We consider the correlation function

$$
\begin{aligned}
S(\boldsymbol{R}) &= \langle \psi_1 | \psi_2 \rangle \\
&= \int d^3\boldsymbol{r}\, \psi_1^*(\boldsymbol{r}) \psi_2(\boldsymbol{r}) \\
&= \int d^3\boldsymbol{r} \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{1}{a_0}\left|\boldsymbol{r}-\frac{\boldsymbol{R}}{2}\right|} \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{1}{a_0}\left|\boldsymbol{r}+\frac{\boldsymbol{R}}{2}\right|} \\
&= \frac{1}{\pi a_0^3} \int d^3\boldsymbol{r} e^{-\frac{1}{a_0}\left|\boldsymbol{r}-\frac{R}{2}\right|} e^{-\frac{1}{a_0}\left|\boldsymbol{r}+\frac{R}{2}\right|} \\
&= \frac{1}{\pi a_0^3} \int d^3\boldsymbol{r}' e^{-\frac{1}{a_0}\left|\boldsymbol{r}'-\boldsymbol{R}\right|} e^{-\frac{1}{a_0} r'}
\end{aligned}
$$

where $\boldsymbol{r}' = \boldsymbol{r} + \dfrac{\boldsymbol{R}}{2}$,

or

$$
S(\boldsymbol{R}) = e^{-\frac{R}{a_0}} \left(1 + \frac{R}{a_0} + 3\frac{R^2}{a_0^2}\right)
$$

We make a plot of $S(R)$ as a function of R.

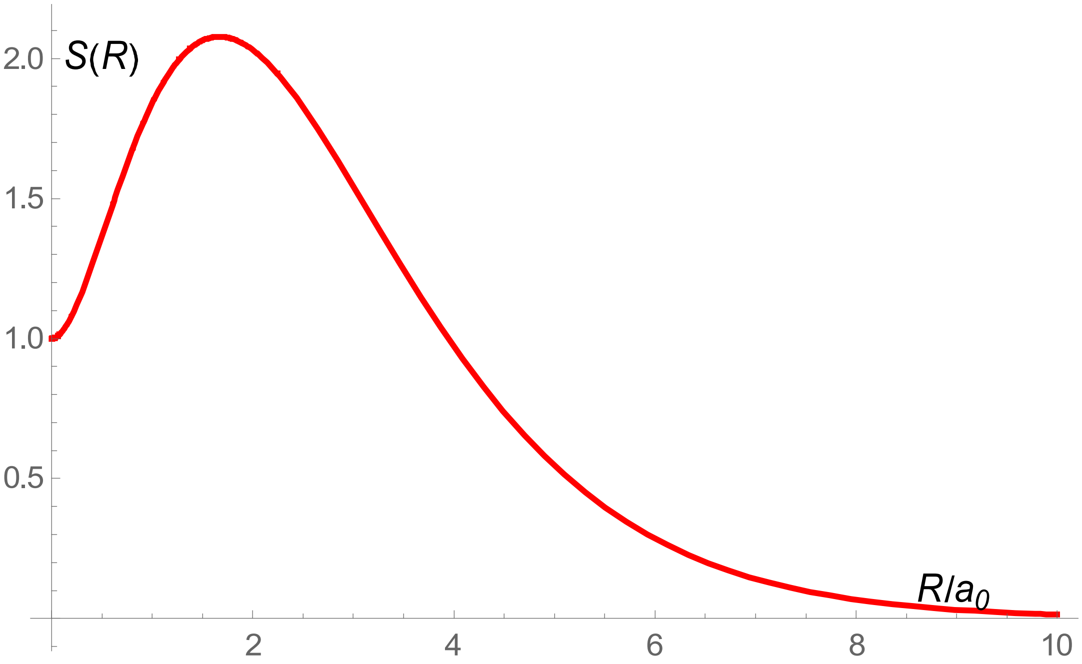


Fig. $S(R)$ vs R/a_0. $a_0 = 0.53$ Å. $dS(R)/dR = 0$ at $R/a_0 = 1.61803$ (i.e. $R = 0.8575$ Å).

(f) Normalization: $\langle\psi_1|\psi_1\rangle = 1$ and $\langle\psi_2|\psi_2\rangle = 1$

$$\begin{aligned}
\langle\psi_1|\psi_1\rangle &= \int d^3\boldsymbol{r}\psi_1^*(\boldsymbol{r})\psi_1(\boldsymbol{r}) \\
&= \int d^3\boldsymbol{r}\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{1}{a_0}\left|\boldsymbol{r}-\frac{\boldsymbol{R}}{2}\right|}\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{1}{a_0}\left|\boldsymbol{r}-\frac{\boldsymbol{R}}{2}\right|} \\
&= \frac{1}{\pi a_0{}^3}\int d^3\boldsymbol{r}e^{-\frac{2}{a_0}\left|\boldsymbol{r}-\frac{\boldsymbol{R}}{2}\right|} \\
&= \frac{1}{\pi a_0{}^3}\int d^3\boldsymbol{r}'e^{-\frac{2}{a_0}|\boldsymbol{r}'|}
\end{aligned}$$

where $\boldsymbol{r}' = \boldsymbol{r} - \dfrac{\boldsymbol{R}}{2}$.

or

$$\langle\psi_1|\psi_1\rangle = 1$$

Similarly we have

$$\langle\psi_2|\psi_2\rangle = 1$$

(g) Calculation of the expectation

$$\begin{aligned}
\langle\psi_e|\psi_e\rangle &= C_e{}^2(\langle\psi_1| + \langle\psi_2|)(|\psi_1\rangle + |\psi_2\rangle) \\
&= C_e{}^2[2 + \langle\psi_1|\psi_2\rangle + \langle\psi_2|\psi_1\rangle] \\
&= C_e{}^2[2 + 2S(R)]
\end{aligned}$$

$$\begin{aligned}
\langle\psi_o|\psi_o\rangle &= C_o{}^2(\langle\psi_1| - \langle\psi_2|)(|\psi_1\rangle - |\psi_2\rangle) \\
&= C_o{}^2[2 - \langle\psi_1|\psi_2\rangle - \langle\psi_2|\psi_1\rangle] \\
&= C_o{}^2[2 - 2S(R)]
\end{aligned}$$

$$\begin{aligned}\langle\psi_e|\psi_o\rangle &= C_eC_o(\langle\psi_1|+\langle\psi_2|)(|\psi_1\rangle-|\psi_2\rangle)\\ &= C_eC_o[-\langle\psi_1|\psi_2\rangle+\langle\psi_2|\psi_1\rangle]\\ &= 0\end{aligned}$$

$$\langle\psi_e|\psi_o\rangle = \langle\psi_o|\psi_e\rangle^* = 0\,.$$

From the normalization condition $\langle\psi_e|\psi_e\rangle = \langle\psi_o|\psi_o\rangle = 1$, we get the constants C_e and C_o as

$$C_e = \frac{1}{\sqrt{2+2S(R)}}$$

$$C_o = \frac{1}{\sqrt{2-2S(R)}}$$

We have

$$\psi_e(\boldsymbol{r}) = \frac{\psi_1(\boldsymbol{r})+\psi_2(\boldsymbol{r})}{\sqrt{2+2S(R)}}$$

$$\psi_O(\boldsymbol{r}) = \frac{\psi_1(\boldsymbol{r})-\psi_2(\boldsymbol{r})}{\sqrt{2-2S(R)}}$$

with

$$\psi_1(\boldsymbol{r}) = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{1}{a_0}\left|\boldsymbol{r}-\frac{1}{2}\boldsymbol{R}\right|}$$

$$\psi_2(\boldsymbol{r}) = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{1}{a_0}e^{-\frac{1}{a_0}\left|\boldsymbol{r}+\frac{1}{2}\boldsymbol{R}\right|}}$$

$$S(R) = e^{-\frac{R}{a_0}}(1+\frac{R}{a_0}+3\frac{R^2}{a_0{}^2})$$

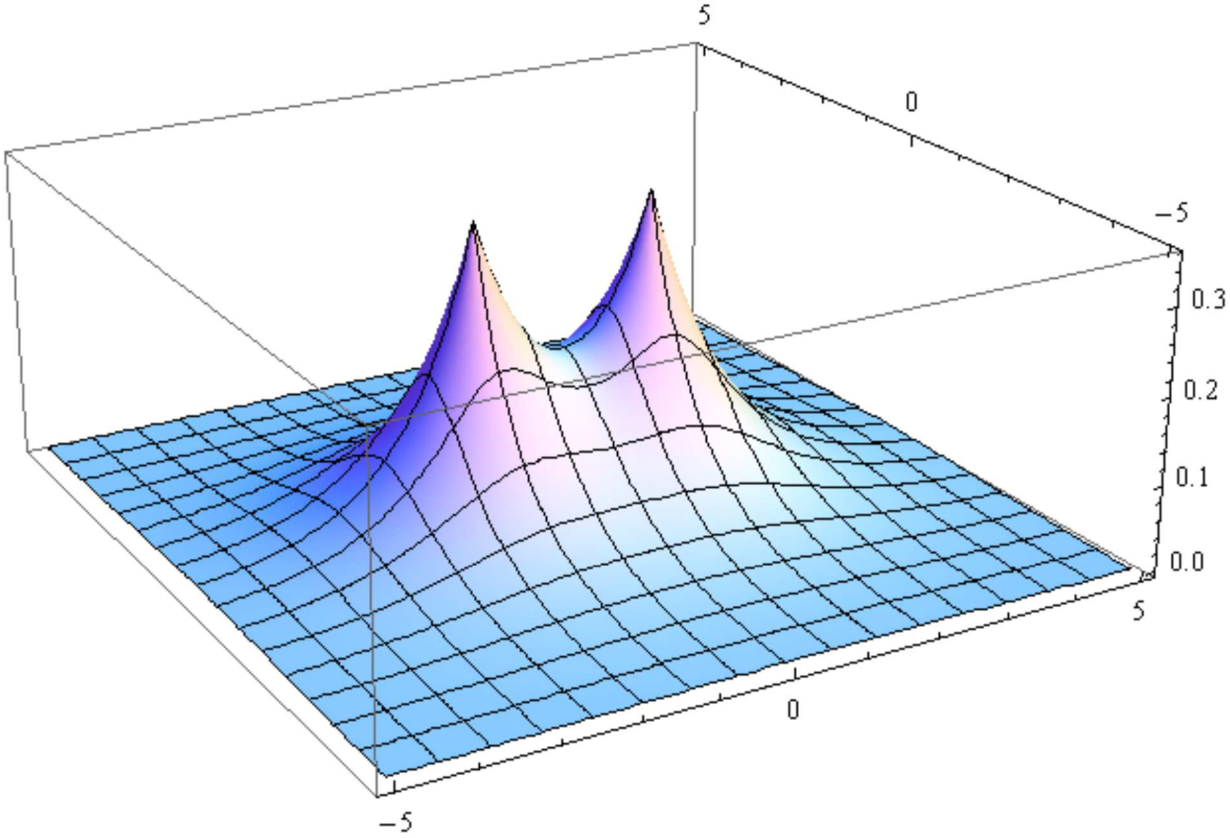
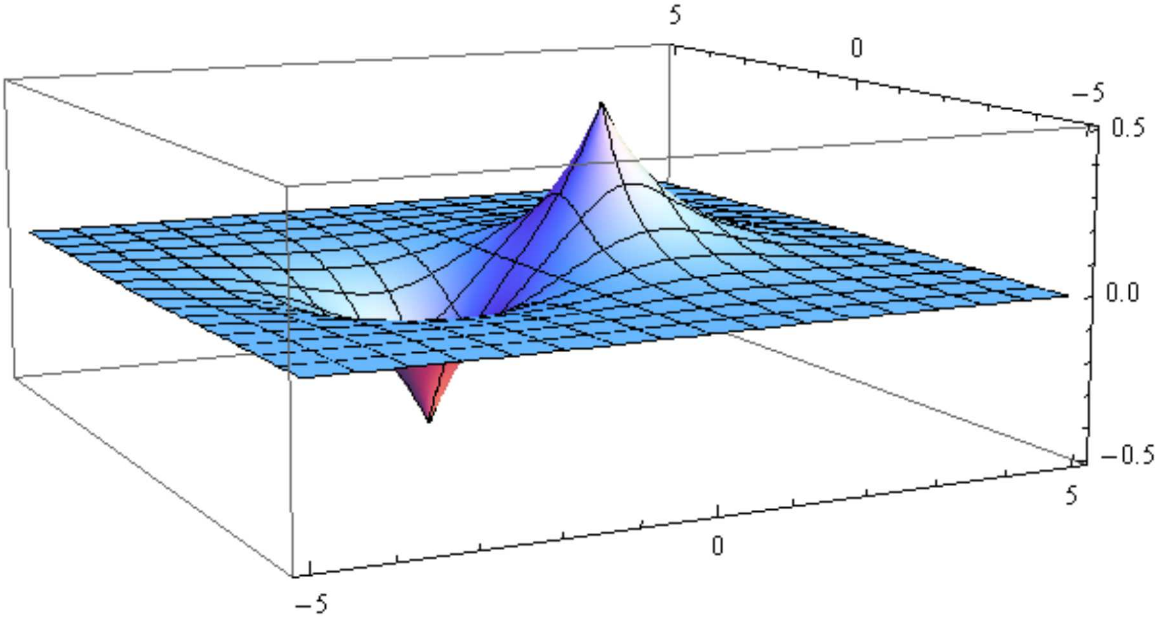


Fig. Plot3D of the wave function $\psi_e(\boldsymbol{r})$. $R/\mathrm{a}_0 = 2.49283$.



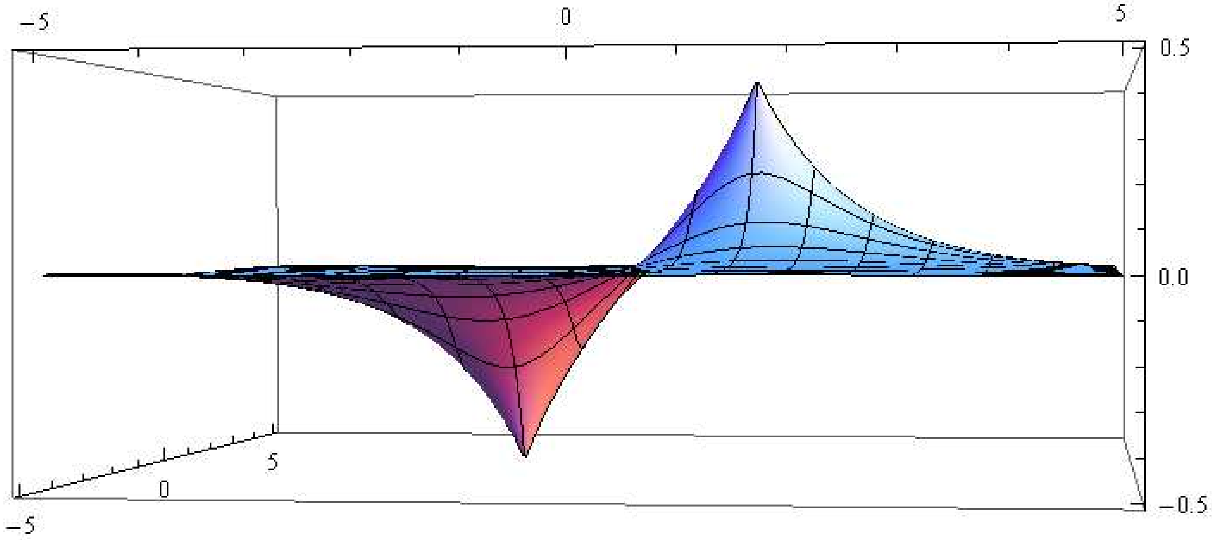


Fig. Plot3D of the wave function $\psi_o(\boldsymbol{r})$. $R/a_0 = 2.49283$.

(h) Matrix element of the Hamiltonian

The matrix element of the Hamiltonian is given by

$$\begin{aligned}\langle\psi_e|\hat{H}|\psi_e\rangle &= C_e^{\,2}(\langle\psi_1| + \langle\psi_2|)\hat{H}(|\psi_1\rangle + |\psi_2\rangle) \\ &= C_e^{\,2}[\langle\psi_1|\hat{H}|\psi_1\rangle + \langle\psi_1|\hat{H}|\psi_2\rangle + \langle\psi_2|\hat{H}|\psi_1\rangle + \langle\psi_2|\hat{H}|\psi_2\rangle]\end{aligned}$$

where

$$\hat{H} = \frac{\hat{\boldsymbol{p}}^2}{2m_e} - \frac{e^2}{\left|\hat{\boldsymbol{r}} - \frac{\boldsymbol{R}}{2}\right|} - \frac{e^2}{\left|\hat{\boldsymbol{r}} + \frac{\boldsymbol{R}}{2}\right|} + \frac{e^2}{|\boldsymbol{R}|}$$

Here we note that

$$\langle\psi_2|\hat{H}|\psi_1\rangle = \langle\psi_1|\hat{\pi}\hat{H}\hat{\pi}|\psi_2\rangle = \langle\psi_1|\hat{H}|\psi_2\rangle$$

$$\langle\psi_2|\hat{H}|\psi_2\rangle = \langle\psi_1|\hat{\pi}\hat{H}\hat{\pi}|\psi_1\rangle = \langle\psi_1|\hat{H}|\psi_1\rangle$$

Then we have

$$\langle\psi_e|\hat{H}|\psi_e\rangle = 2C_e^{\,2}[\langle\psi_1|\hat{H}|\psi_1\rangle + \langle\psi_1|\hat{H}|\psi_2\rangle]$$

Similarly, we get

$$\begin{aligned}\langle\psi_o|\hat{H}|\psi_o\rangle &= C_o^{\,2}(\langle\psi_1| - \langle\psi_2|)\hat{H}(|\psi_1\rangle - |\psi_2\rangle) \\ &= 2C_o^{\,2}[\langle\psi_1|\hat{H}|\psi_1\rangle - \langle\psi_1|\hat{H}|\psi_2\rangle]\end{aligned}$$

Then

$$\frac{\langle\psi_e|\hat{H}|\psi_e\rangle}{\langle\psi_e|\psi_e\rangle} = \frac{\langle\psi_1|\hat{H}|\psi_1\rangle + \langle\psi_1|\hat{H}|\psi_2\rangle}{1+S(R)}$$

and

$$\frac{\langle\psi_o|\hat{H}|\psi_o\rangle}{\langle\psi_o|\psi_o\rangle} = \frac{\langle\psi_1|\hat{H}|\psi_1\rangle - \langle\psi_1|\hat{H}|\psi_2\rangle}{1-S(R)}$$

where

$$\langle\psi_1|\hat{H}|\psi_1\rangle = E_{1s} + \frac{e^2}{R}e^{-\frac{2R}{a_0}}(1+\frac{R}{a_0})]$$

$$\langle\psi_1|\hat{H}|\psi_2\rangle = (E_{1s} + \frac{e^2}{R})S(\boldsymbol{R}) - \frac{e^2}{a_0}(1+\frac{R}{a_0})e^{-\frac{R}{a_0}}$$

$$\langle\psi_1|\frac{e^2}{\left|\hat{\boldsymbol{r}} + \frac{\boldsymbol{R}}{2}\right|}|\psi_1\rangle = \frac{e^2}{R}[1 - e^{-\frac{2R}{a_0}}(1+\frac{R}{a_0})]$$

$$\langle\psi_1|\frac{e^2}{\left|\hat{\boldsymbol{r}} - \frac{\boldsymbol{R}}{2}\right|}|\psi_2\rangle = \frac{e^2}{a_0}e^{-\frac{R}{a_0}}(1+\frac{R}{a_0})$$

(i) Bonding orbital and anti-bonding orbital

$$E_e(R) = \frac{\langle\psi_e|\hat{H}|\psi_e\rangle}{\langle\psi_e|\psi_e\rangle} = \frac{\langle\psi_1|\hat{H}|\psi_1\rangle + \langle\psi_1|\hat{H}|\psi_2\rangle}{1+S(R)},$$

$$E_o(R) = \frac{\langle \psi_o | \hat{H} | \psi_o \rangle}{\langle \psi_o | \psi_o \rangle} = \frac{\langle \psi_1 | \hat{H} | \psi_1 \rangle - \langle \psi_1 | \hat{H} | \psi_2 \rangle}{1 - S(R)},$$

where

$$\langle \psi_1 | \hat{H} | \psi_1 \rangle = E_{1s} + \frac{e^2}{R} e^{-\frac{2R}{a_0}} (1 + \frac{R}{a_0}),$$

$$\langle \psi_1 | \hat{H} | \psi_2 \rangle = (E_{1s} + \frac{e^2}{R}) S(R) - \frac{e^2}{a_0}(1 + \frac{R}{a_0}) e^{-\frac{R}{a_0}},$$

$$S(R) = e^{-\frac{R}{a_0}} (1 + \frac{R}{a_0} + 3\frac{R^2}{a_0^2}).$$

We make a plot of $E_e(R)$ and $E_o(R)$ below. $E_e(R)$ has a local minimum at $R/a_0 = 2.49283$. $R = 1.3212$ Å. The local minimum value is -15.3634 eV.

(i) For both $|\psi_e\rangle$ and $|\psi_O\rangle$ states, the energy at large R is simply the hydrogen atom as is expected. At very small R ($<<a_0$), the energy of both states becomes positive and very large due to the strong proton-proton Coulomb repulsion.

(ii) For intermediate inter-nuclear separation, the even-parity and odd-parity states have different energies. The minimum in the even-parity state energy is indicative of an attraction that leads to a stable molecule with a separation distance t $R = 2.49283\ a_0$ (or $R = 1.3212$ Å). The energy of the odd-parity state has no minimum and is repulsive at all distances R, implying that a system in this state will dissociate into a bound hydrogen atom and an isolated proton.

We call the $|\psi_e\rangle$ state as a **bonding orbital** and the odd-parity $|\psi_O\rangle$ state as an **antibonding orbital**

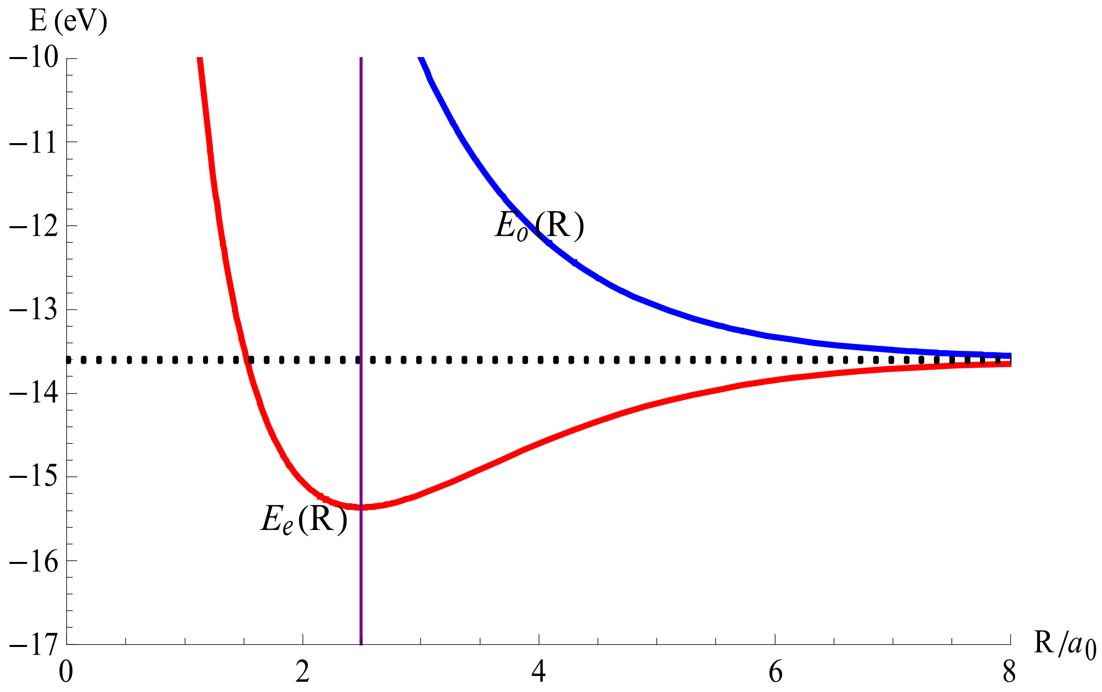


Fig. Plot of $E_e(R)$ and $E_o(R)$ as a function of R/a_0. $E_e(R)$ has a local minimum at $R/a_0 = 2.49283$. R = 1.3212 Å. The local minimum value is -15.3634 eV. The dashed line denotes the ground-state energy of the hydrogen atom.

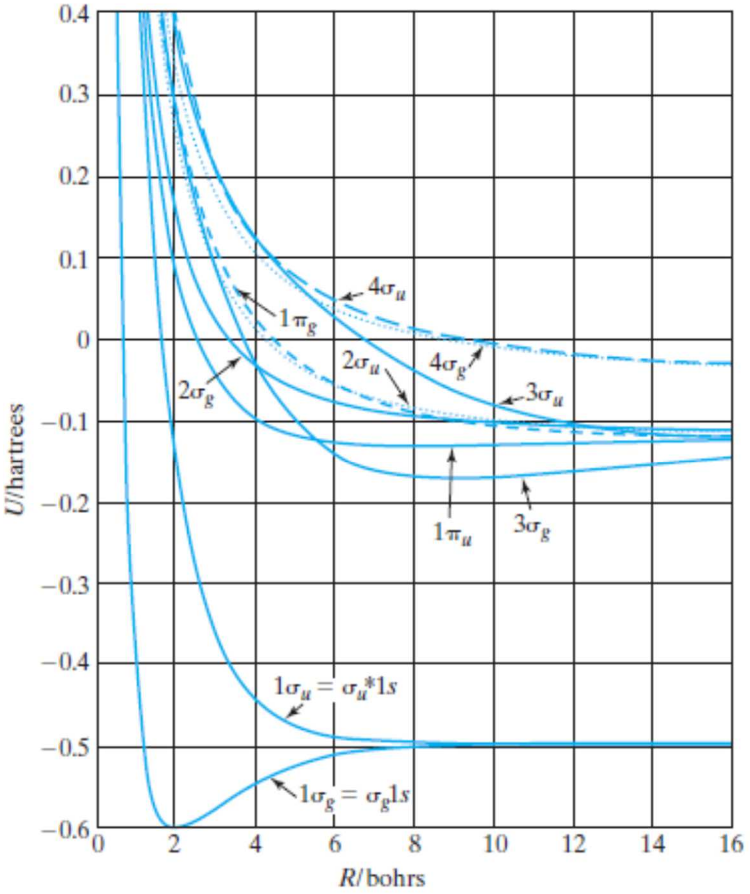


Fig. Energy level of several H_2^+ electronic states. 1 hartree = 627.5 kcal/mol = 27.211 eV. The ground state is $|1\sigma_g\rangle$ and the first excited state is $|1\sigma_u\rangle$

(j) ContourPlot

We make a ContourPlot of $\psi_e(\boldsymbol{r})$ and $\psi_O(\boldsymbol{r})$ in the *x*-*y* plane, where $R = 2.49283\ a_0$.

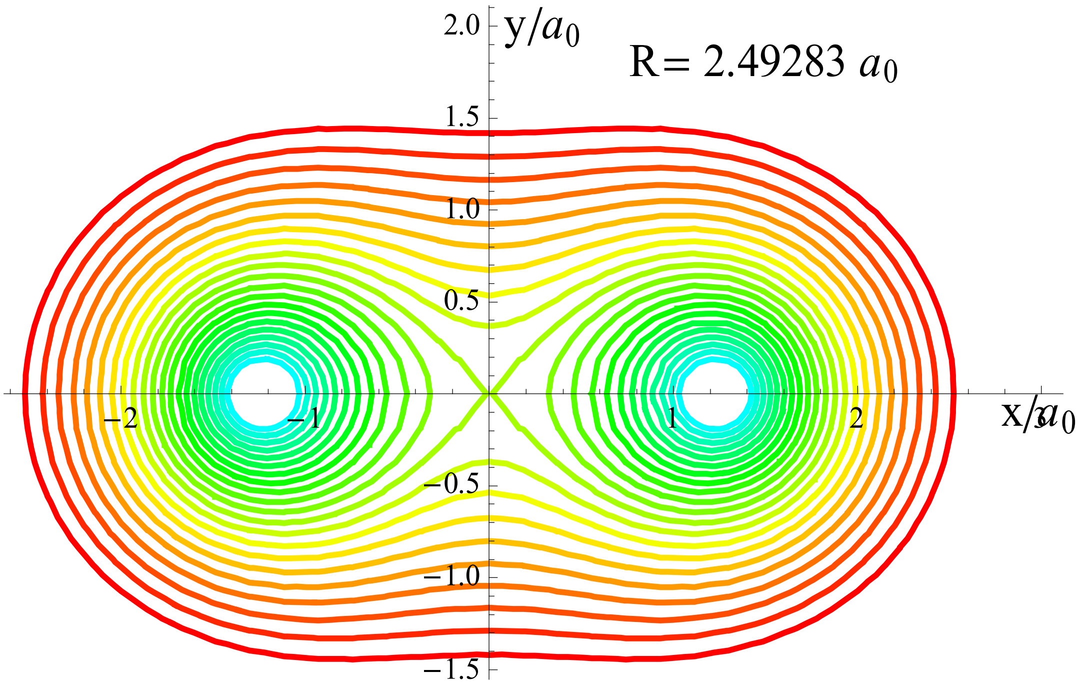


Fig. ContourPlot of $\psi_e(\boldsymbol{r})$ in the *x*-*y* plane, where $R = 2.49283\ a_0$.

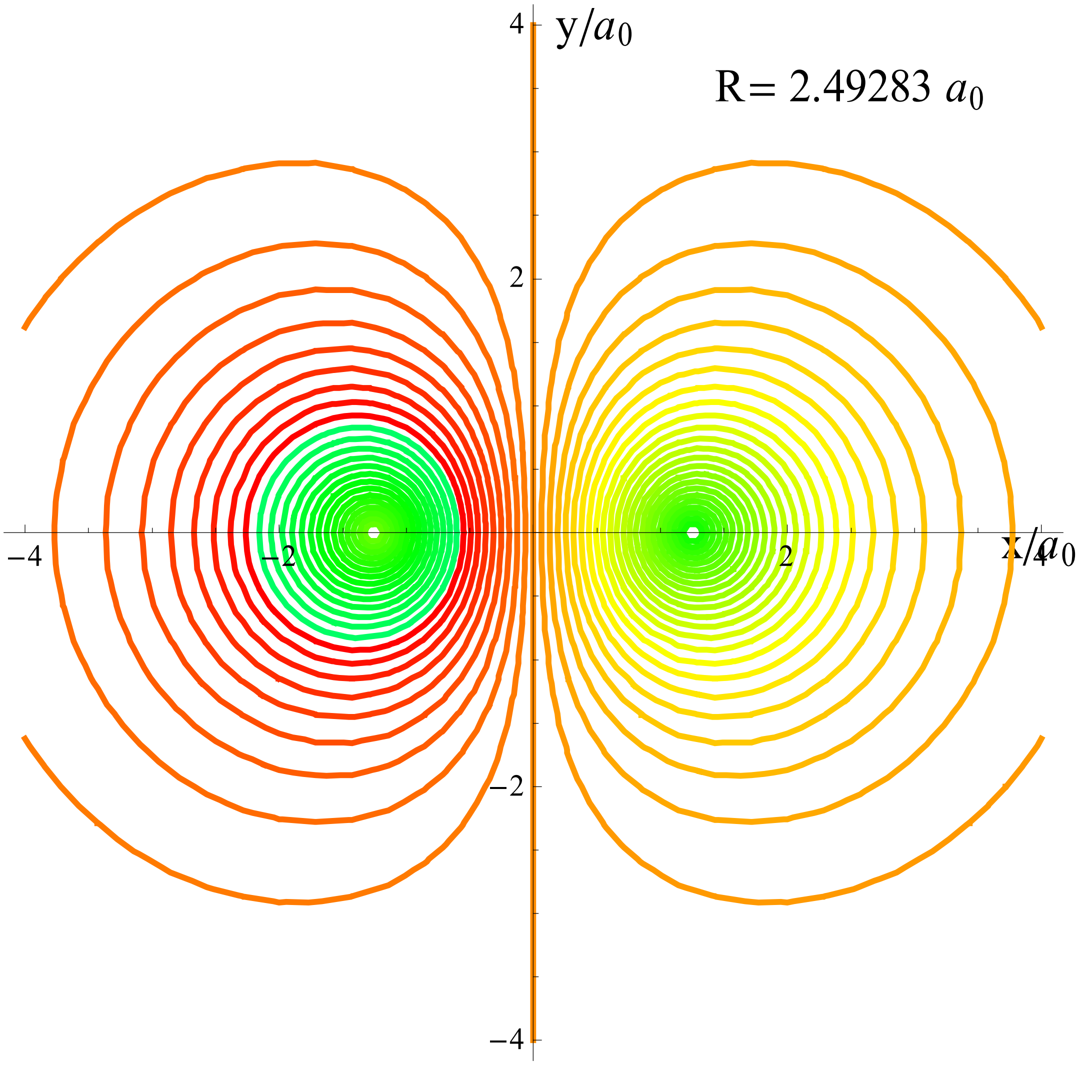


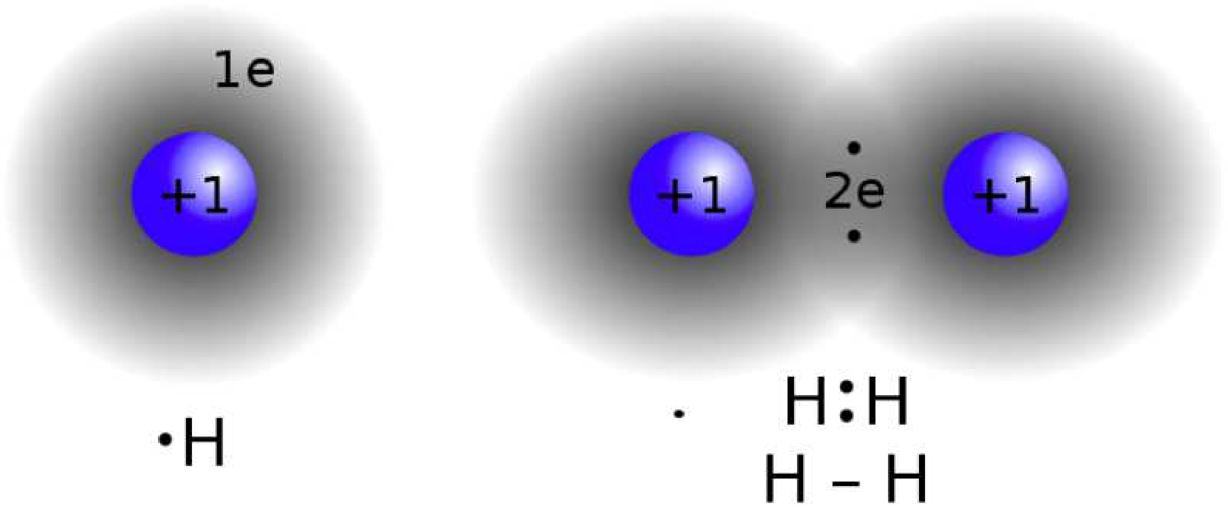
Fig. ContourPlot of $\psi_O(\boldsymbol{r})$ in the *x*-*y* plane, where $R = 2.49283\ a_0$.

8. Pauli exclusion principle and exchange interaction

In hydrogen molecules, there are two protons and two electrons. It is very complicated to solve the eigenvalue problems for the system as a function of co-ordinates and spins of 4 particles. the coordinates of four particles. Instead of solving this problem, we use the approximation. To this end, we neglect the kinetic energy of the protons. We also neglect the interaction between electrons. In this case the problem is reduced to a simple problem of one electron moving in the presence of two protons (fixed). We find the eigenstate of one electron. Next, based on the Pauli exclusion principle, we take into account of the spin symmetry of the two spins, so that the total wave function is antisymmetric under the exchange of the sites. This method is called the **linear combination of atomic orbitals (LCAO)**

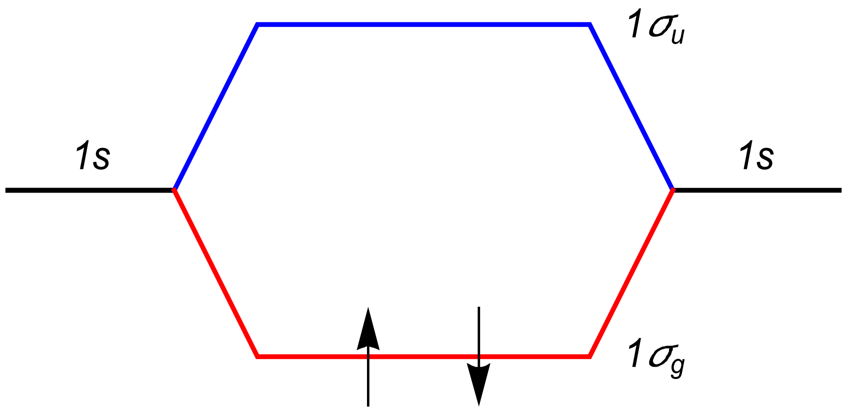
9. Two electrons system (hydrogen molecule H_2)

Hydrogen molecule (H_2)



In the molecule H_2, the hydrogen atoms share the two electrons via covalent bonding. Covalency is greatest between atoms of similar electronegativities. Thus, covalent bonding does not necessarily require that the two atoms be of the same elements, only that they be of comparable electronegativity. Covalent bonding that entails sharing of electrons over more than two atoms is said to be delocalized.

(a) Ground state: the total energy is $\approx 2E_e$ (singlet)



Spatial wave function: $|\psi_e\rangle_1|\psi_e\rangle_2$ (symmetric state)

Spin wave function: $\frac{1}{\sqrt{2}}(\alpha\beta-\beta\alpha)$ ($S=0$ state; antisymmetric state))

leading to the antisymmetric wave function

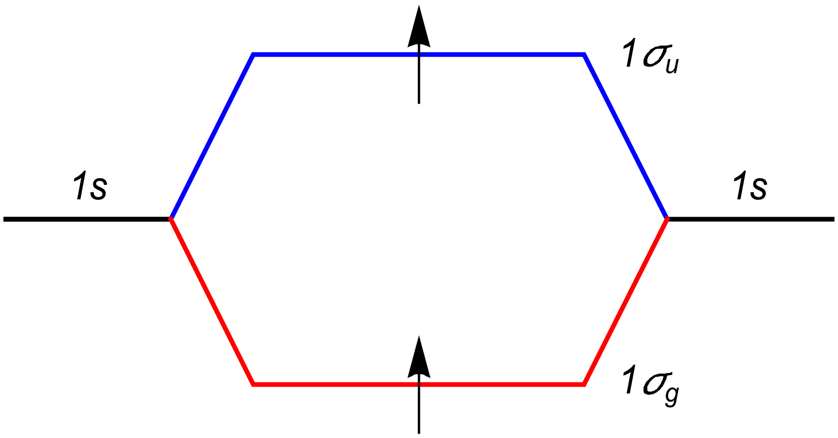
$B^1\Sigma_u^{\ +}$:

$$|\psi_e\rangle|\psi_e\rangle\frac{1}{\sqrt{2}}(\alpha\beta-\beta\alpha)$$

because of the fermion.

(b) The first excited state: the total energy is $\approx E_e+E_0$ (triplet)

The first excited state for the two particle system is



According to the Hund's rule, the spin direction of the particle in the state $|1\sigma_u\rangle$ is parallel to that of the particle in the state $|1\sigma_g\rangle$

State with two particles:

$|\psi_e\rangle\alpha$ and $|\psi_o\rangle\alpha$

Spatial wave function: $\frac{1}{\sqrt{2}}[|\psi_o\rangle_1|\psi_e\rangle_2-|\psi_e\rangle_1|\psi_o\rangle_2]$ (anti-symmetric state)

Spin wave function: $\frac{1}{\sqrt{2}}(\alpha\beta+\beta\alpha)$, $\alpha\alpha$, and $\beta\beta$

($S=1$ state; triplet, symmetric state)

leading to the antisymmetric wave function

$b^3\Sigma_u^+$:

$$\frac{1}{\sqrt{2}}[|\psi_o\rangle_1|\psi_e\rangle_2 - |\psi_e\rangle_1|\psi_o\rangle_2]\left\{\begin{matrix}\alpha\alpha \\ \frac{1}{\sqrt{2}}(\alpha\beta+\beta\alpha) \\ \beta\beta\end{matrix}\right\}$$

because of the fermion.

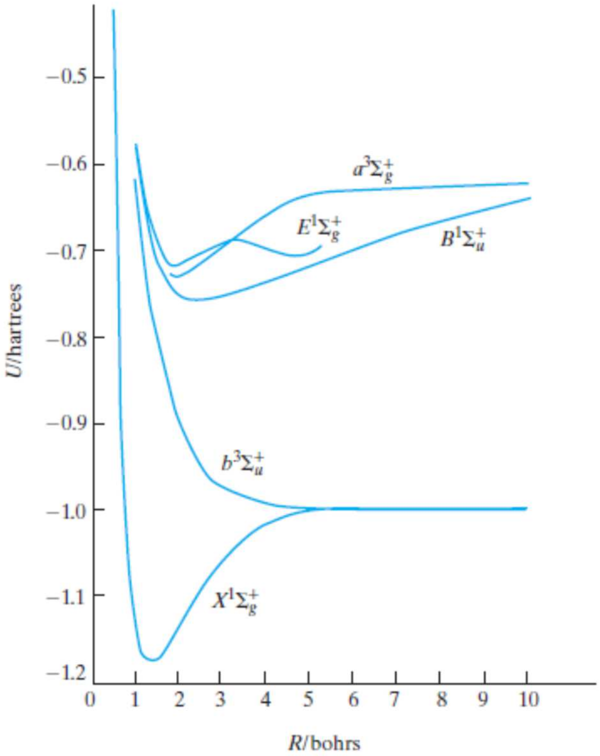


Fig. Energy diagram for some electronic states of H_2, including the ground state (singlet) and the first excited state (triplet).

10. Molecular term symbol

It has the general form:

$$^{2S+1}\Lambda^{(\pm)}{}_{\Omega,(g/u)}$$

where

- S is the total spin quantum number
- Λ is the projection of the orbital angular momentum along the internuclear axis
- Ω is the projection of the total angular momentum along the internuclear axis
- u/g is the effect of the point group operation ***i***
- +/− is the reflection symmetry along an arbitrary plane containing the internuclear axis

11. Exchange interaction between two spins (Heisenberg-type)

According to the quantum mechanics, the addition of spin angular momentum (with spin 1.2) leads to

$$D_{1/2} \times D_{1/2} = D_1 + D_0$$

(a) $S = 1$ **state (symmetric state); 3 states**

$$|\chi_s\rangle = \begin{cases} |++\rangle \\ \frac{1}{\sqrt{2}}[|+-\rangle + |-+\rangle] \\ |--\rangle \end{cases}$$

For the symmetric spatial wave function with energy eigenvalue (E_s), the spin state should be antisymmetric one;

(b) $S = 0$ state (antisymmetric state)

$$|\chi_a\rangle = \frac{1}{\sqrt{2}}[|+-\rangle - |-+\rangle]$$

Here we use the Dirac exchange operator,

$$\hat{P}_{12} = \frac{1}{2}(1 + \hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_2)$$

where $\hat{\boldsymbol{\sigma}}$ is the Pauli operator; $\hat{\boldsymbol{S}}_1 = \frac{\hbar}{2}\hat{\boldsymbol{\sigma}}_1$ and $\hat{\boldsymbol{S}}_2 = \frac{\hbar}{2}\hat{\boldsymbol{\sigma}}_2$. The total spin operator is given by

$$\hat{\boldsymbol{S}} = \frac{\hbar}{2}(\hat{\boldsymbol{\sigma}}_1 + \hat{\boldsymbol{\sigma}}_2)$$

Note that

$$\begin{aligned}\hat{\boldsymbol{S}}^2 &= \left(\frac{\hbar}{2}\right)^2 (\hat{\boldsymbol{\sigma}}_1 + \hat{\boldsymbol{\sigma}}_2)^2 \\ &= \left(\frac{\hbar}{2}\right)^2 (6 + 2\hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_2) \\ &= \left(\frac{\hbar}{2}\right)^2 [6 + 2(2\hat{P}_{12} - 1)] \\ &= \hbar^2(\hat{P}_{12} + \hat{1})\end{aligned}$$

Thus we have

$$\hat{P}_{12}\left|\chi_s\right\rangle = \left|\chi_s\right\rangle, \qquad \hat{P}_{12}\left|\chi_a\right\rangle = -\left|\chi_a\right\rangle$$

We now consider the effective spin Hamiltonian

$$\hat{H} = \alpha + \beta\hat{P}_{12} = \alpha + \beta\frac{1}{2}(1 + \hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_2)$$

$$\hat{H}\left|\chi_s\right\rangle = (\alpha + \beta\hat{P}_{12})\left|\chi_s\right\rangle = (\alpha + \beta)\left|\chi_s\right\rangle = E_s\left|\chi_s\right\rangle$$

$$\hat{H}\left|\chi_a\right\rangle = (\alpha + \beta\hat{P}_{12})\left|\chi_a\right\rangle = (\alpha - \beta)\left|\chi_s\right\rangle = E_a\left|\chi_a\right\rangle$$

leading to the relation

$$\alpha = \frac{E_s + E_a}{2}, \qquad \beta = \frac{E_s - E_a}{2}$$

Thus we get the effective spin Hamiltonian

$$\begin{aligned}\hat{H} &= \alpha + \beta\frac{1}{2}(1+\hat{\boldsymbol{\sigma}}_1\cdot\hat{\boldsymbol{\sigma}}_2)\\ &= \frac{3E_s+E_a}{4}+\frac{E_s-E_a}{4}(\hat{\boldsymbol{\sigma}}_1\cdot\hat{\boldsymbol{\sigma}}_2)\ .\\ &= \frac{3E_s+E_a}{4}+\frac{E_s-E_a}{\hbar^2}(\hat{\boldsymbol{S}}_1\cdot\hat{\boldsymbol{S}}_2)\end{aligned}$$

The exchange energy J between two spins is obtained as

$$J = \frac{E_s - E_a}{\hbar^2} < 0 \qquad \text{(ferromagnetic interaction).}$$

The binding depends on the relative spin orientation not because there are strong magnetic dipole forces between the spins, but because the Pauli principle modifies the distribution of charges according to the spin orientation. This spin dependent Coulomb energy is called the exchange interaction.

12. Hund’s rule

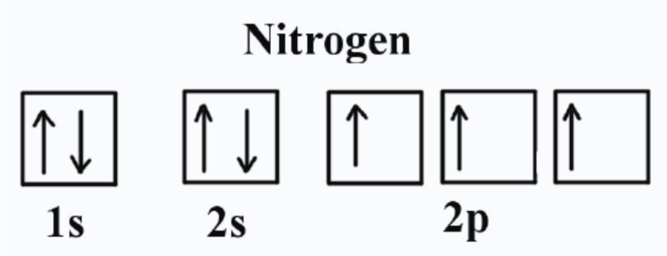
The 1s orbitals should be filled before 2s orbitals, because the 1s orbitals have a lower value of n, and thus a lower energy. What about the three different 2p orbitals? In what order should they be filled? The answer to this question involves Hund's rule.

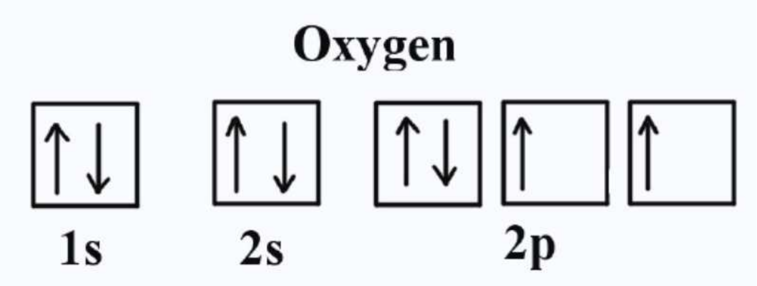
Hund's rule states that:

1. Every orbital in a sublevel is singly occupied before any orbital is doubly occupied.
2. All of the electrons in singly occupied orbitals have the same spin (to maximize total spin).

According to the first rule, electrons always enter an empty orbital before they pair up. Electrons are negatively charged and, as a result, they repel each other. Electrons tend to minimize repulsion by occupying their own orbitals, rather than sharing an orbital with another electron. Furthermore, quantum-mechanical calculations have shown that the electrons in singly occupied orbitals are less effectively screened or shielded from the nucleus. Electron shielding is further discussed in the next section.

For the second rule, unpaired electrons in singly occupied orbitals have the same spins. Technically speaking, the first electron in a sublevel could be either "spin-up" or "spin-down." Once the spin of the first electron in a sublevel is chosen, however, the spins of all of the other electrons in that sublevel depend on that first spin. To avoid confusion, scientists typically draw the first electron, and any other unpaired electron, in an orbital as "spin-up."



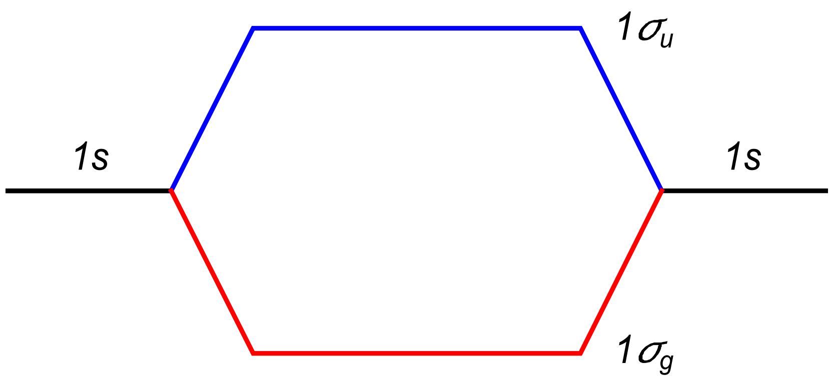


13. Further discussion on the energy diagram

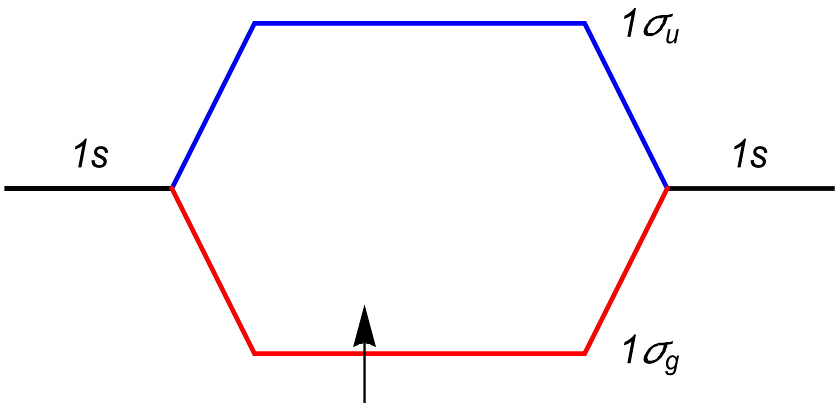
We consider the wave function and the energy diagram of the hydrogen molecule H_2 (two-body problem) using the energy diagram of the H_2+ ion (one-electron energy diagram) and the Pauli's exclusion principle for the fermion.

We note that from two atomic orbitals we can build two molecular orbitals. In general, from *N* atomic orbitals we can build *N* molecular orbitals. There are two electrons to accommodate, and both can enter 1σg by pairing their spins, as required by the Pauli principle. The ground-state configuration is therefore $1g\sigma^2$ and the atoms are joined by a bond consisting of an electron pair in a bonding σ orbital. This approach shows that an electron pair, which was the focus of Lewis's account of chemical bonding, represents the maximum number of electrons that can enter a bonding molecular orbital. The same argument explains why He does not form diatomic molecules. Each He atom contributes a 1s orbital, so 1σg and 1σu molecular orbitals can be constructed. Although these orbitals differ in detail from those in H_2, their general shapes are the same and we can use the same qualitative energy level diagram in the discussion. There are four electrons to accommodate. Two can enter the $1\sigma_g$ orbital, but then it is full, and the next two must enter the $1\sigma_u$ orbital. The ground electronic configuration of He^2 is therefore $1\sigma_g{}^2 1\sigma_u{}^2$.

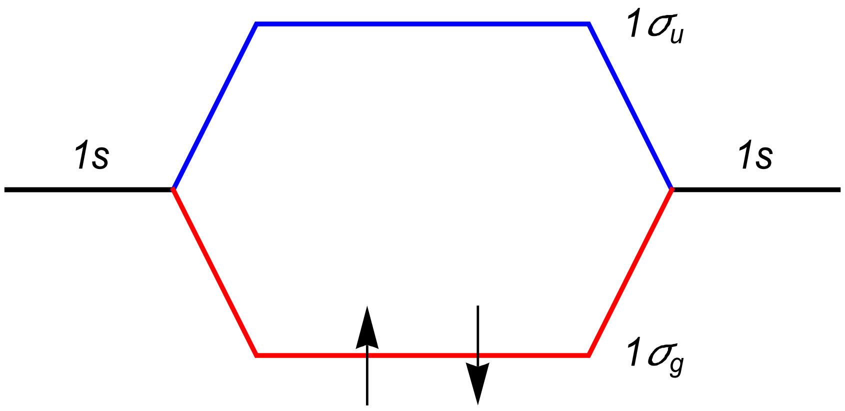
We see that there is one bond and one anti-bond. Because $1\sigma_u$ is raised in energy relative to the separate atoms more than $1\sigma_g$ is lowered, an He^2 molecule has a higher energy than the separated atoms, so it is unstable relative to them.



(a) One electron system



(b) The ground state for the two electrons

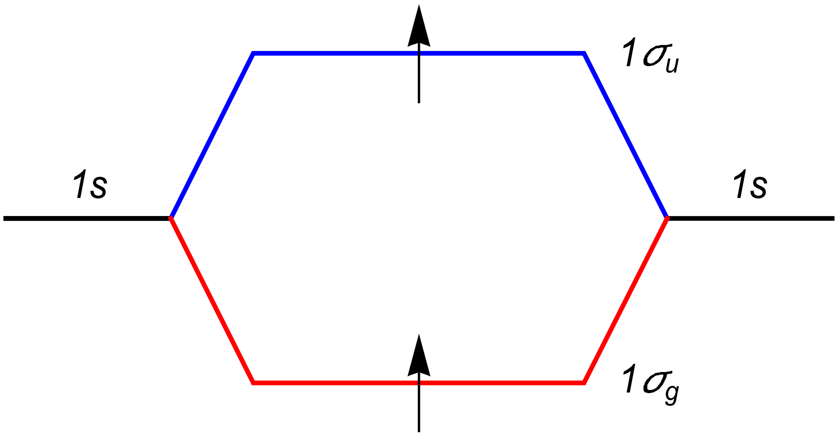


The ground state: The spin state is a singlet (antisymmetric).

$$\left|1\sigma_g\right\rangle_1 \left|1\sigma_g\right\rangle_2 \left|S=0(\text{singlet})\right\rangle$$

$$|S=0(\text{singlet})\rangle = \frac{1}{\sqrt{2}}[|\alpha\rangle_1|\beta\rangle_2 - |\beta\rangle_1|\alpha\rangle_2]$$

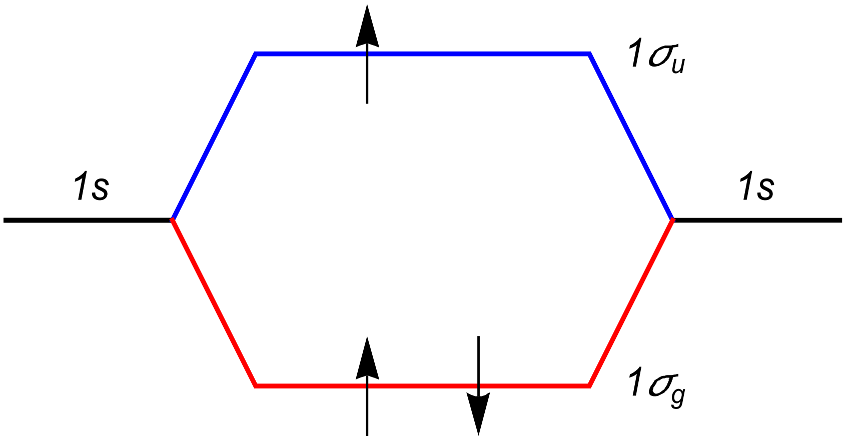
(b) The first excited state with two electrons



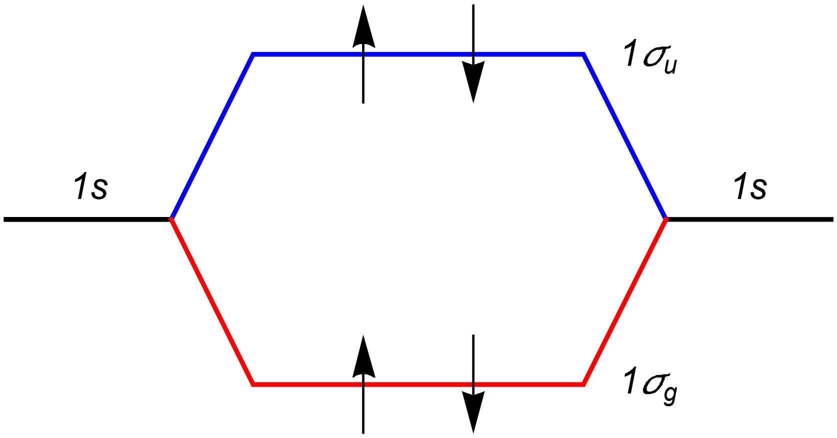
According to the Hund's rule, the spin direction of the upper state is parallel to that of the lower state. In other words, the spin state of $|1\sigma_u\rangle$ should be the same as that of the $|1\sigma_g\rangle$,

$$\frac{1}{\sqrt{2}}[|1\sigma_g\rangle_1|1\sigma_u\rangle_2 - |1\sigma_u\rangle_1|1\sigma_g\rangle_2|S=1(\text{triplet})\rangle$$

(c) The states with three particles



(d) The state with four particles (closed shell)



14. Hybridization

We assume that two atoms A and B (atoms A and B are the same) are located on the z axis. When the position of atom A is close to that of the atom B, we consider the molecular orbits of atomic orbitals, 1s, 2s, 2p_x, 2p_y, 2p_z.

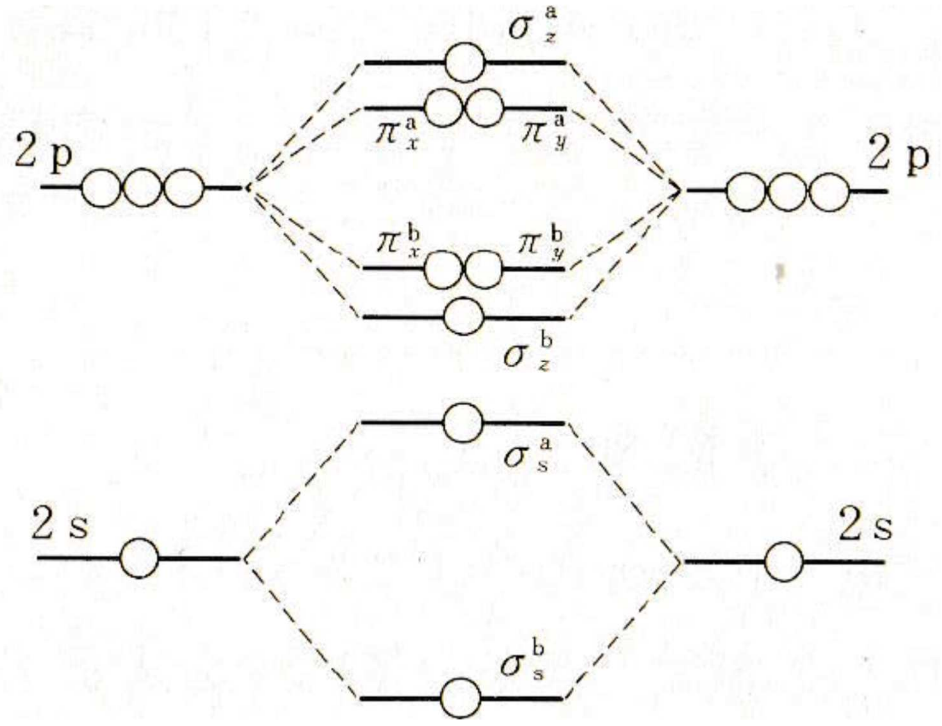


Fig. Energy levels without the $s - p_z$ interaction. The energy level of 2p state is much higher than that of 2s state.

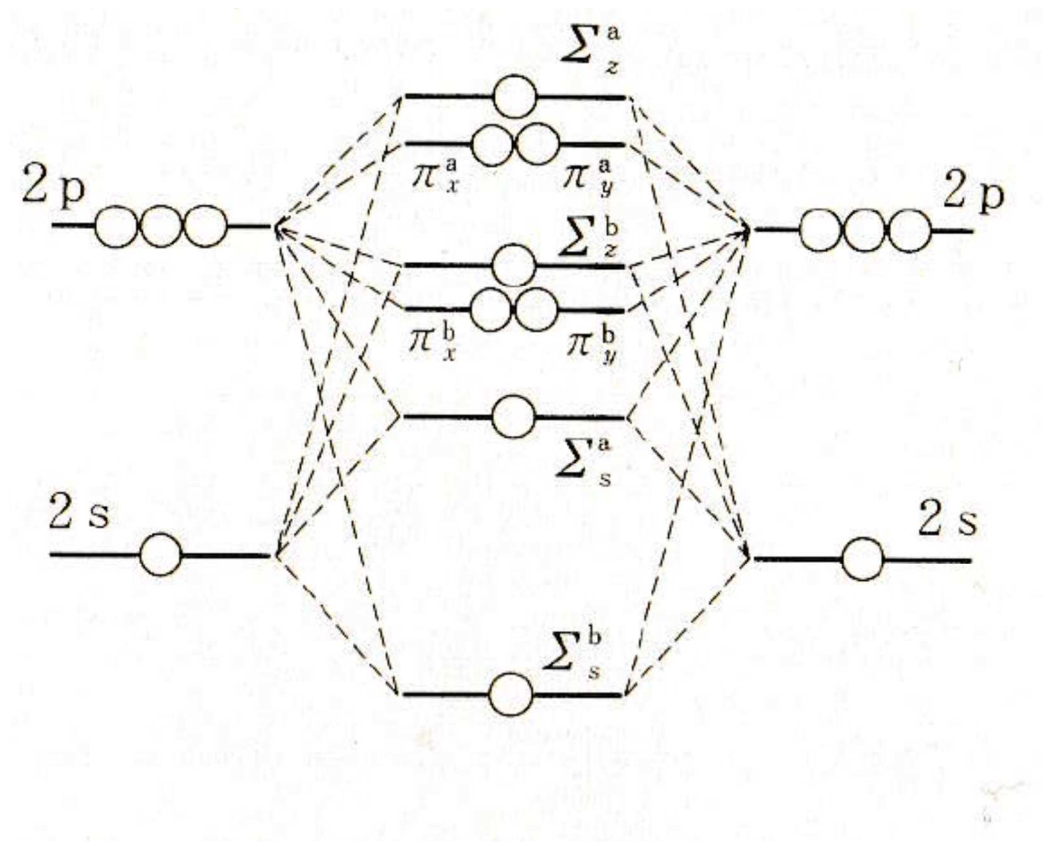
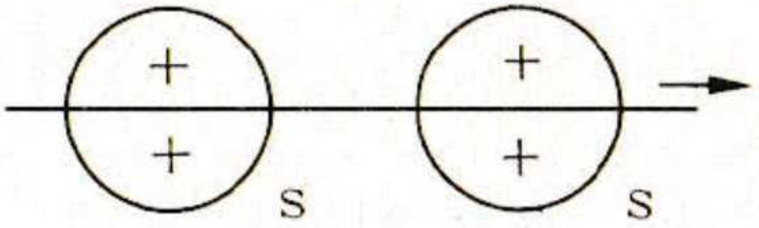


Fig. Energy levels with strong $s - p_z$ interaction. The energy level of 2*p* state is not so higher than that of 2*s* state.

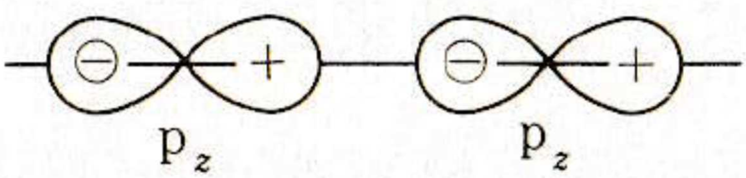
(a) 2*s* and 2*s* orbits



$$\left|\sigma_s{}^b\right\rangle = \frac{1}{\sqrt{2+2S_{ss}}}[\left|2s_A\right\rangle + \left|2s_B\right\rangle] \qquad \text{(bonding)}$$

$$\left|\sigma_s{}^a\right\rangle = \frac{1}{\sqrt{2-2S_{ss}}}[\left|2s_A\right\rangle - \left|2s_B\right\rangle] \qquad \text{(anti-bonding)}$$

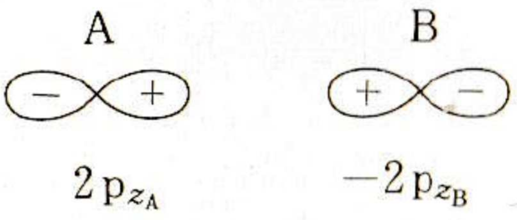
(b) $2p_z$ and $2p_z$ orbits



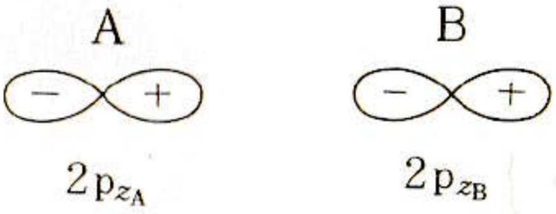
$$\left|\sigma_z{}^b\right\rangle = \frac{1}{\sqrt{2-2S_{zz}}}[\left|2p_{zA}\right\rangle - \left|2p_{zB}\right\rangle] \qquad \text{(bonding)}$$

$$\left|\sigma_z{}^a\right\rangle = \frac{1}{\sqrt{2+2S_{ss}}}[\left|2p_{zA}\right\rangle + \left|2p_{zB}\right\rangle] \qquad \text{(anti-bonding)}$$

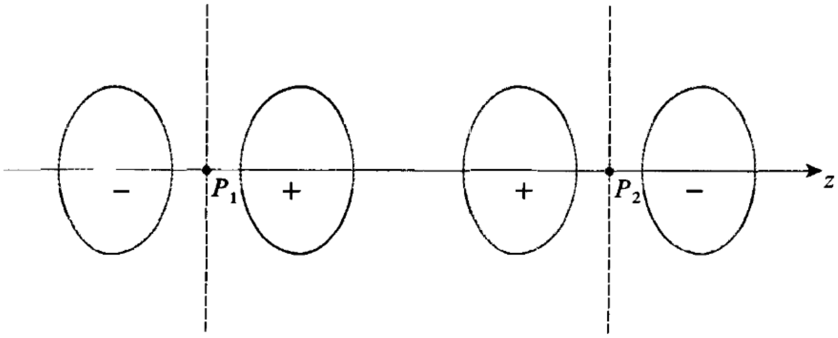
Note that for the bonding [$\sigma_g(2p_z)$ -state]

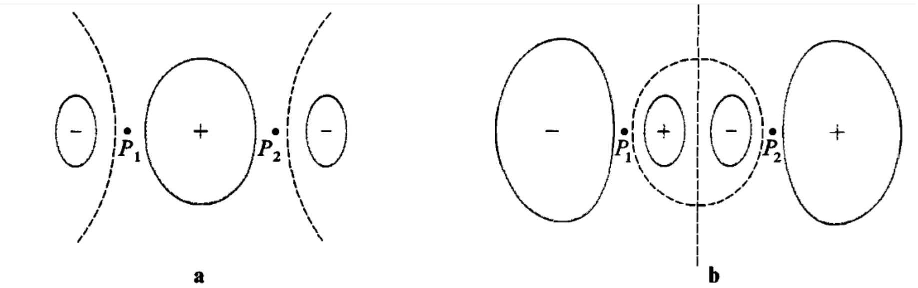


and for the anti-bonding [$\sigma_u{}^*(2p_z)$ -state]



((**Note**)) Cohen-Tannoudji et al. Quantum Mechanics

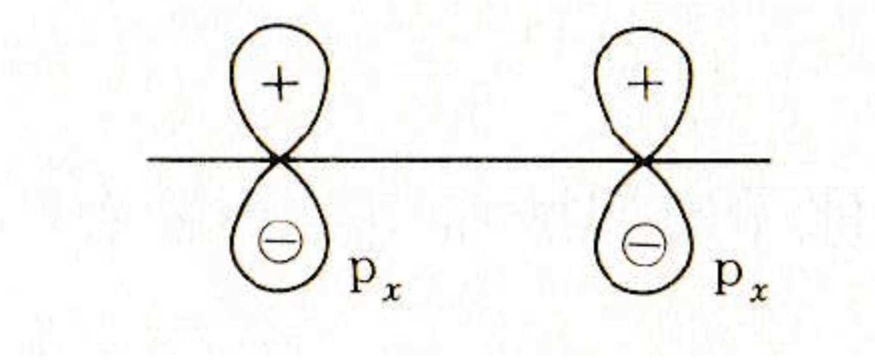




$\sigma_g(2p_z)$ -state $\sigma_u{}^*(2p_z)$ -state

Fig. Schematic representation of the $2p_z$ atomic orbitals centered at P_1 and P_2 and used as a basis for constructing the excited molecular orbitals $\sigma_g(2p_z)$ and $\sigma_u{}^*(2p_z)$ (note the sign convention chosen). (Cohen-Tannoudji et al. Quantum Mechanics): (a)

(c) $2p_y$ and $2p_y$ orbits



$$\left|\pi_x{}^b\right\rangle = \frac{1}{\sqrt{2+2S_{xx}}}[\left|2p_{xA}\right\rangle + \left|2p_{xB}\right\rangle]$$

$$\left|\pi_x{}^a\right\rangle = \frac{1}{\sqrt{2-2S_{xx}}}[\left|2p_{xA}\right\rangle - \left|2p_{xB}\right\rangle]$$

$$\left|\pi_y{}^b\right\rangle = \frac{1}{\sqrt{2+2S_{yy}}}[\left|2p_{yA}\right\rangle + \left|2p_{yB}\right\rangle]$$

$$\left|\pi_y{}^a\right\rangle = \frac{1}{\sqrt{2-2S_{yy}}}[\left|2p_{yA}\right\rangle - \left|2p_{yB}\right\rangle]$$

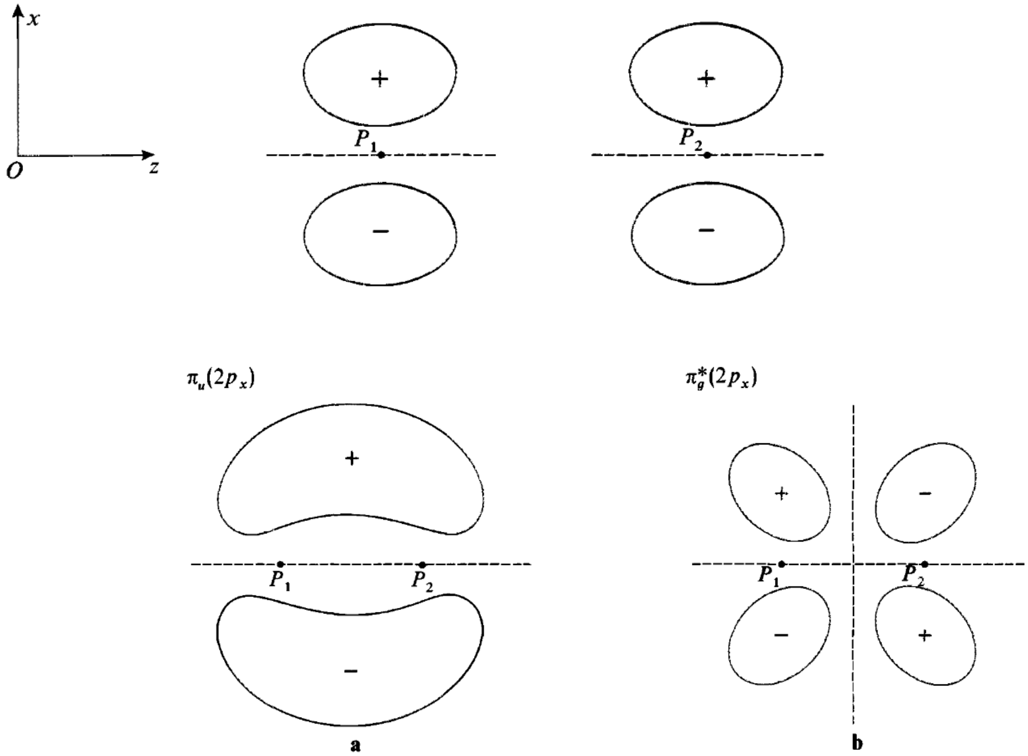


Fig. Schematic representation of the atomic orbitals $2p_x$ centered at P_1 and P_2 (the *Oz* axis is chosen along P_1P_2) and used as a basis for constructing the excited molecular orbitals $\pi_u(2p_x)$ and $\pi_g{}^*(2p_x)$.

15. Molecular orbits

σMO's

σ indicates the z-component of the orbital angular momentum is $|m| = 0$.

$$|1s\sigma_u\rangle \approx |1s_a\rangle + |1s_b\rangle,$$

$$|1s\sigma_g\rangle \approx |1s_a\rangle - |1s_b\rangle$$

$$|2s\sigma_u\rangle \approx |2s_a\rangle + |2s_b\rangle$$

$$|2s\sigma_g\rangle \approx |2s_a\rangle - |2s_b\rangle$$

$|2p_z\sigma_g\rangle \approx |2p_{za}\rangle - |2p_{zb}\rangle$ (note the minus sign for $|2p_z\sigma_g\rangle$)

$|2p_z\sigma_u\rangle \approx |2p_{za}\rangle + |2p_{zb}\rangle$ (note the plus sign for $|2p_z\sigma_u\rangle$)

π MO's

π indicates the z-component of the orbital angular momentum is $|m| = 0$.

$$|2p_x\pi_u\rangle \approx |2p_{xa}\rangle + |2p_{xb}\rangle$$

$$|2p_x\pi_g\rangle \approx |2p_{xa}\rangle - |2p_{xb}\rangle$$

$$|2p_y\pi_u\rangle \approx |2p_{ya}\rangle + |2p_{yb}\rangle$$

$$|2p_y\pi_g\rangle \approx |2p_{ya}\rangle - |2p_{yb}\rangle$$

16. Orbital hybridization: two possible representation; $\sigma - \pi$ and equivalent-orbital models

Molecules with multiple bonds or multiple lone pairs can have orbitals represented in terms of sigma and pi symmetry or equivalent orbitals. The sigma and pi representation of Erich Hückel is the more common one compared to the equivalent orbital representation of Linus Pauling. The two have mathematically equivalent total many-electron wave functions, and are related by a unitary transformation of the set of occupied molecular orbitals. This is a very important concept. In my opnion, the orbital model is much easier for one to vusialize the covalent bonding.

((Example)) sp hybridization (orbital)

Using the following example, we understand that the two models are equivalent.

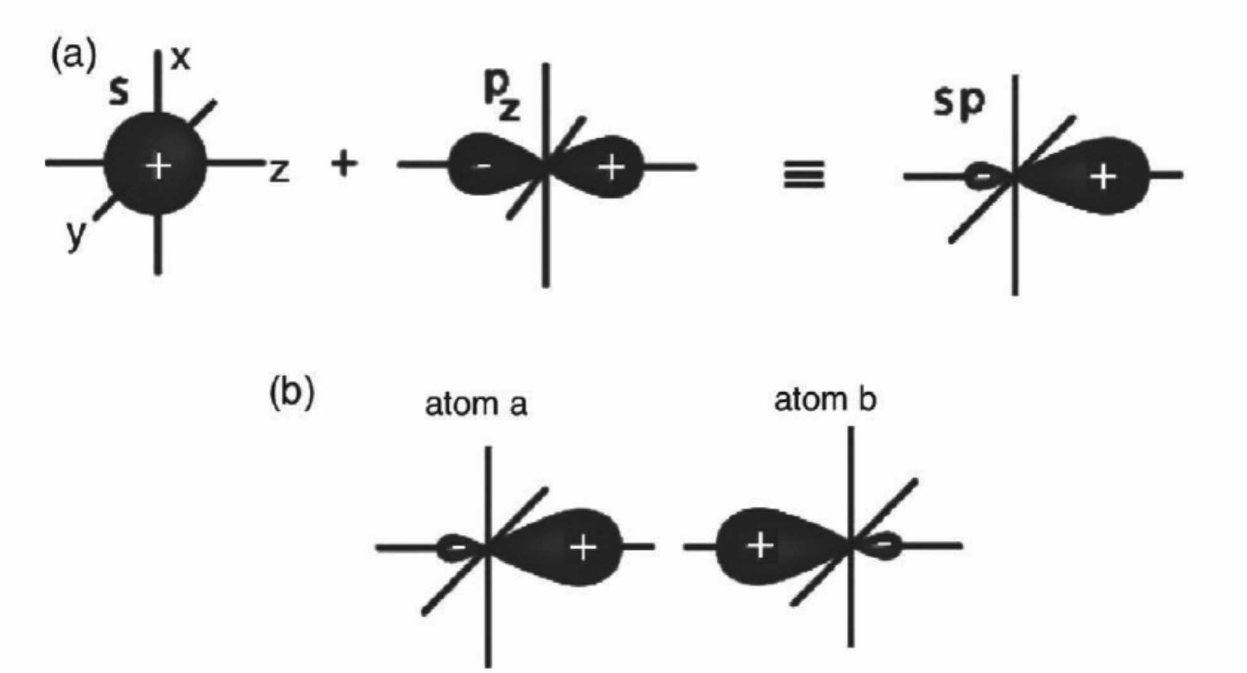


Fig. (a) sp hybrid orbital. (b) Molecular orbital made from a LCAO's ($\sigma-\pi$ model)

Note that

$$\begin{aligned}|\phi\rangle &= (|1s_a\rangle + |1s_b\rangle) + c(|2p_{za}\rangle - |2p_{zb}\rangle) \\ &= |1\sigma_g\rangle + c|2p_z\sigma_g\rangle\end{aligned} \qquad (\sigma-\pi \text{ model})$$

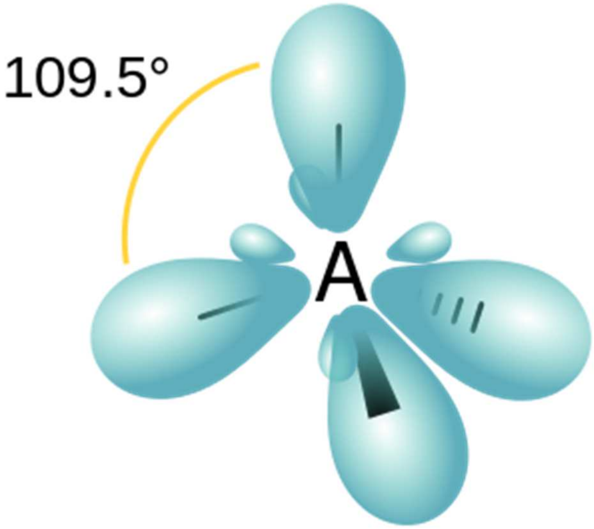
$$|\psi\rangle = |1s\rangle + c|2p_z\rangle \qquad \text{(orbital model)}$$

The wave functions of the four states (sp hybridization) are given by

$$|\psi_1\rangle = \frac{1}{\sqrt{2}}|s\rangle + \frac{1}{\sqrt{2}}|p_z\rangle$$

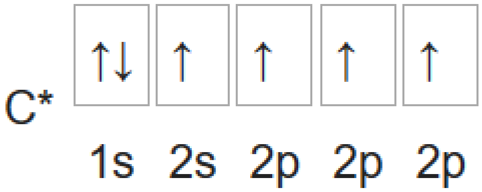
$$|\psi_2\rangle = \frac{1}{\sqrt{2}}|s\rangle - \frac{1}{\sqrt{2}}|p_z\rangle$$

17. sp^3 hybridization for carbon: CH_4 (methane)

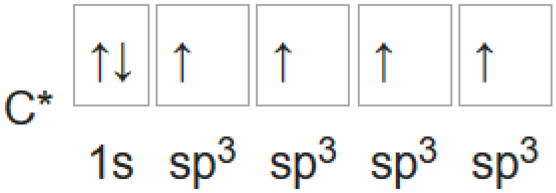


Carbon’s ground state configuration is $(1s)^2(2s)^2(2p)^2$ (based on the Hund’s rule)

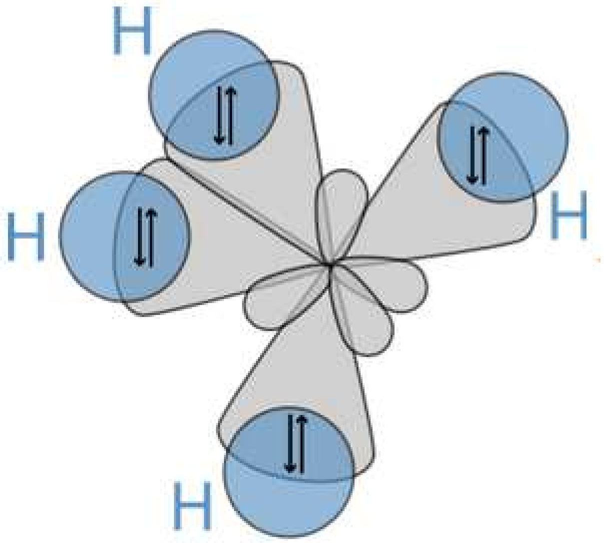
The carbon atom can use its two singly occupies p-type orbitals, to form two covalent bonds. The carbon atoms can also four covalent bonds, by an excitation of an electron from the doubly occupied 2s orbital to the empty 2p orbital, producing four singly occupied orbitals.;

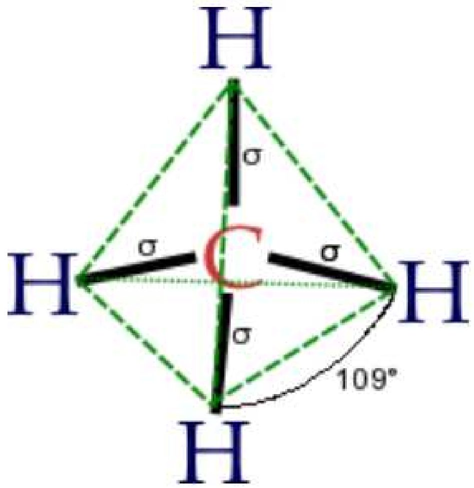


Quantum mechanically, the lowest energy is obtained if the four bonds are equivalent, which requires that they are formed from equivalent orbitals on the carbon. A set of four equivalent orbitals can be obtained that are linear combinations of the valence-shell (core orbitals are almost never involved in bonding) s and p wave functions, which are the four sp^3 hybrids.



In CH$_4$, four sp^3 hybrid orbitals are overlapped by hydrogen 1s orbitals, yielding four σ (sigma) bonds (that is, four single covalent bonds) of equal length and strength.





https://en.wikipedia.org/wiki/Orbital_hybridisation

The wave functions of the four states (sp^3 hybridization) are given by

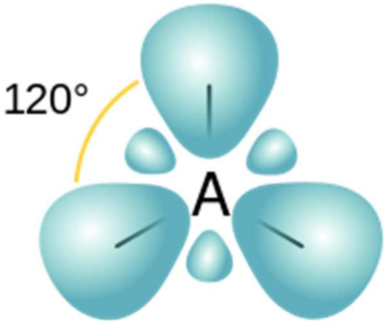
$$|\psi_1\rangle = \frac{1}{2}|s\rangle + \frac{1}{2}|p_x\rangle + \frac{1}{2}|p_y\rangle + \frac{1}{2}|p_z\rangle$$

$$|\psi_2\rangle = \frac{1}{2}|s\rangle - \frac{1}{2}|p_x\rangle - \frac{1}{2}|p_y\rangle + \frac{1}{2}|p_z\rangle$$

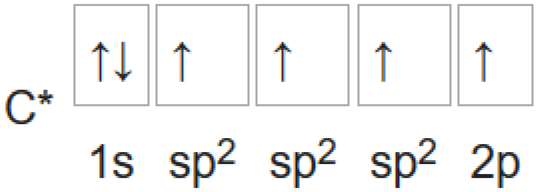
$$|\psi_3\rangle = \frac{1}{2}|s\rangle - \frac{1}{2}|p_x\rangle + \frac{1}{2}|p_y\rangle - \frac{1}{2}|p_z\rangle$$

$$|\psi_4\rangle = \frac{1}{2}|s\rangle + \frac{1}{2}|p_x\rangle - \frac{1}{2}|p_y\rangle - \frac{1}{2}|p_z\rangle$$

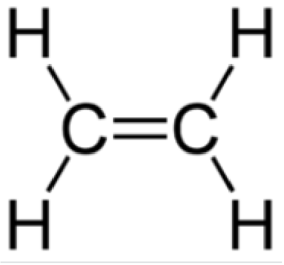
18. sp^2 hybridization: C_2H_4



Ethene (C_2H_4) has a double bond between the carbons. For this molecule, carbon sp^2 hybridises, because one π (pi) bond is required for the double bond between the carbons and only three σ bonds are formed per carbon atom. In sp^2 hybridisation the 2s orbital is mixed with only two of the three available 2p orbitals (Hund's rule)



forming a total of three sp^2 orbitals with one remaining p orbital. In ethylene (ethene) the two carbon atoms form a σ bond by overlapping two sp^2 orbitals and each carbon atom forms two covalent bonds with hydrogen by s–sp^2 overlap all with 120° angles. The π bond between the carbon atoms perpendicular to the molecular plane is formed by 2p–2p overlap. The hydrogen–carbon bonds are all of equal strength and length.



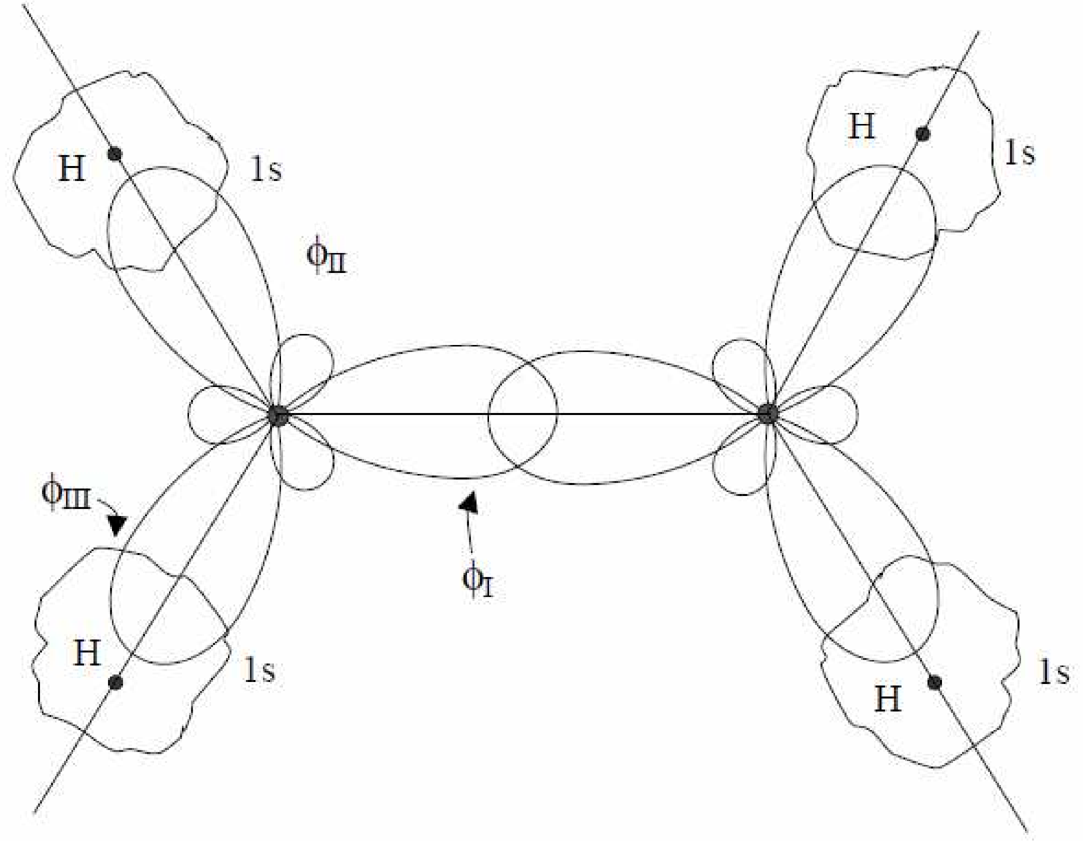
https://en.wikipedia.org/wiki/Orbital_hybridisation

The wave functions of the there states (sp^2 hybridization) are given by

$$|\phi_I\rangle = \frac{1}{\sqrt{3}}|2s\rangle + \sqrt{\frac{2}{3}}|2p_x\rangle$$

$$|\phi_{II}\rangle = \frac{1}{\sqrt{3}}|2s\rangle - \frac{1}{\sqrt{6}}|2p_x\rangle + \frac{1}{\sqrt{2}}|2p_y\rangle$$

$$|\phi_{III}\rangle = \frac{1}{\sqrt{3}}|2s\rangle - \frac{1}{\sqrt{6}}|2p_x\rangle - \frac{1}{\sqrt{2}}|2p_y\rangle$$



19. sp hybridization: C_2H_2

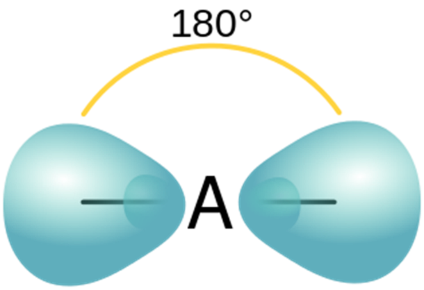
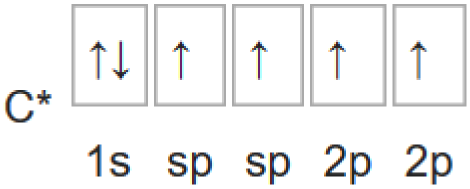


Fig. Two sp orbitals.

In this model, the 2s orbital is mixed with only one of the three p orbitals (Hund's rule)



resulting in two sp orbitals and two remaining p orbitals. The chemical bonding in acetylene (ethyne) (C_2H_2) consists of sp–sp overlap between the two carbon atoms forming a σ bond and two additional π bonds formed by p–p overlap. Each carbon also bonds to hydrogen in a σ s–sp overlap at 180° angles.

https://en.wikipedia.org/wiki/Orbital_hybridisation

20. Metallic bond

Metallic bonding is a type of chemical bonding that arises from the electrostatic attractive force between conduction electrons (in the form of the free electron Fermi gas) and positively charged metal ions. It may be described as the sharing of free electrons among a lattice of positively charged ions (cations). Metallic bonding accounts for many physical properties of metals, such as thermal and electrical conductivity, and so on. According to the Heisenberg's principle of uncertainty, the kinetic energy of the electron is approximated by

$$E_k = \frac{1}{2m} p^2 \approx \frac{\hbar^2}{2m(\Delta x)^2}$$

since $\Delta p \Delta x \approx p \Delta x \approx \hbar$. As the uncertainty of position Δx increases, the kinetic energy tends to decrease, lowering the total energy of the system.

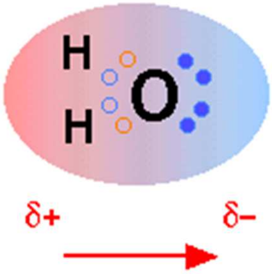
21. Hydrogen bond

A hydrogen bond is an electrostatic attraction between two polar groups that occurs when a hydrogen (H) atom, covalently bound to a highly electronegative atom such as nitrogen (N), oxygen (O), or fluorine (F), experiences the electrostatic field of another highly electronegative atom nearby.

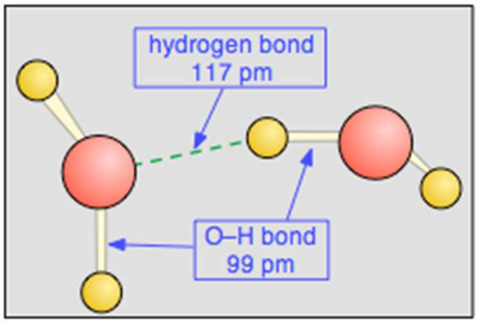
Hydrogen bonds can occur between molecules (intermolecular) or within different parts of a single molecule (intramolecular). Depending on the nature of the donor and acceptor atoms which constitute the bond, their geometry, and environment, the energy of a hydrogen bond can vary between 1 and 40 kcal/mol. This makes them somewhat stronger than a van der Waals interaction, and weaker than covalent or ionic bonds. This type of bond can occur in inorganic molecules such as water and in organic molecules like DNA and proteins.

((Hydrogen bond in water))

The H_2O molecule is electrically neutral, but the positive and negative charges are not distributed uniformly. The electronic (negative) charge is concentrated at the oxygen end of the molecule, owing partly to the nonbonding electrons, and to oxygen's high nuclear charge which exerts stronger attractions on the electrons. This charge displacement constitutes an electric dipole,



The negative end of one water molecule will tend to orient itself so as to be close to the positive end of another molecule that happens to be nearby. The strength of this *dipole-dipole attraction* is less than that of a normal chemical bond, and so it is completely overwhelmed by ordinary thermal motions in the gas phase. However, when the H_2O molecules are crowded together in the liquid, these attractive forces exert a very noticeable effect, which we call (somewhat misleadingly) *hydrogen bonding*. And at temperatures low enough to turn off the disruptive effects of thermal motions, water freezes into ice in which the hydrogen bonds form a rigid and stable network.



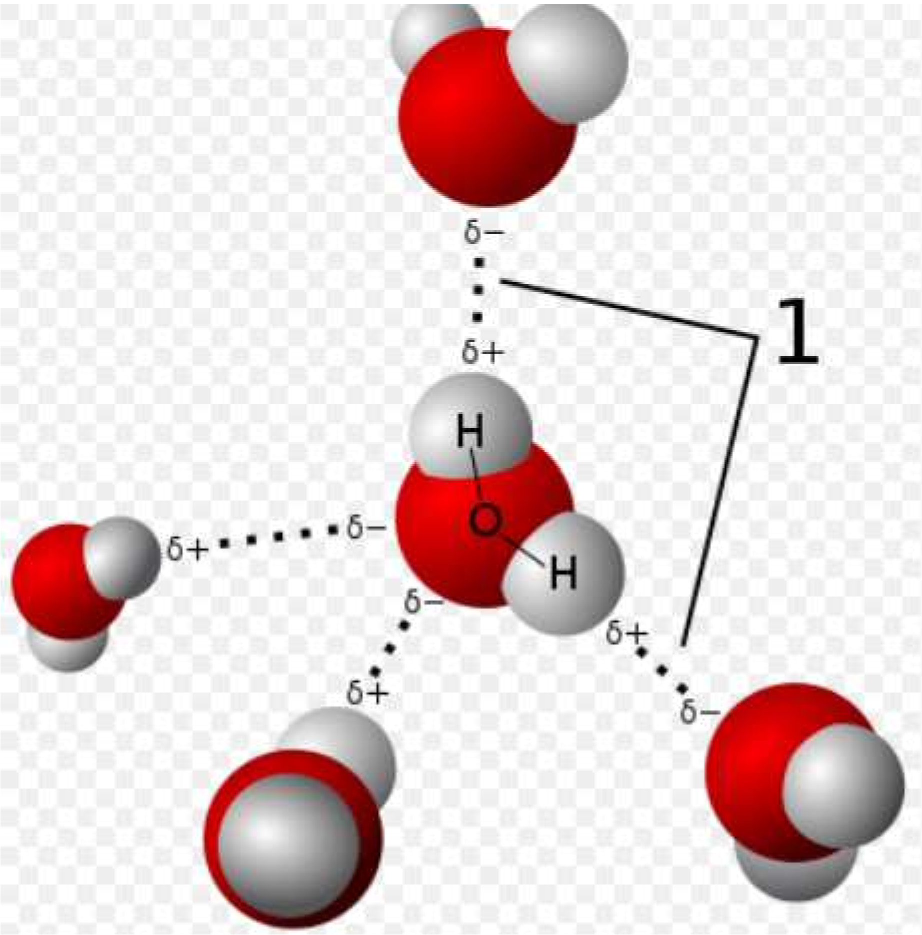


Fig. Hydrogen bond of water H_2O

The most ubiquitous and perhaps simplest example of a hydrogen bond is found between water molecules. In a discrete water molecule, there are two hydrogen atoms and one oxygen atom. Two molecules of water can form a hydrogen bond between them; the simplest case, when only two molecules are present, is called the water dimer and is often used as a model system. When more molecules are present, as is the case with liquid water, more bonds are possible because the oxygen of one water molecule has two lone pairs of electrons, each of which can form a hydrogen bond with a hydrogen on another water molecule. This can repeat such that every water molecule is H-bonded with up to four other molecules, as shown in the figure (two through its two lone pairs, and two through its two hydrogen atoms). Hydrogen bonding strongly affects the crystal structure of ice, helping to create an open hexagonal lattice. The density of ice is less than the density of water at the same temperature; thus, the solid phase of water floats on the liquid, unlike most other substances.

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APPENDIX-I Polarizability

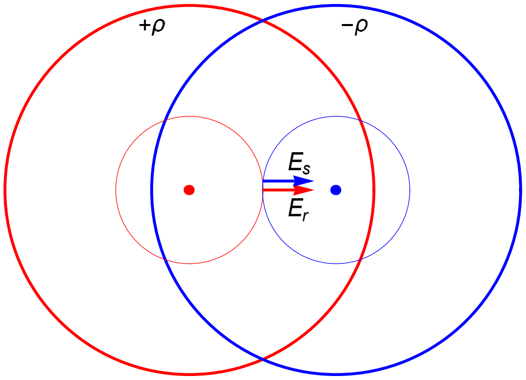
$$F = eE \qquad \text{[dyne = erg/cm]},$$

$$p = \alpha E = er\,.$$

Then we get

$$\alpha = \frac{er}{E} = \frac{e^2 r}{eE} = [\frac{erg \cdot cm^2}{erg / cm}] = [cm^3]\,.$$

We have two spheres, each of radius *a*, one of which has volume charge density $+\rho$ and the other of which has density $-\rho$. The vector from the center of the positive sphere to the center of the negative sphere is *d*. The two spheres have a region of overlap and we want the electric field within this region.



We see that the electric field inside a uniformly positively charged sphere is (restoring the vector notation)

$$E_r = \frac{4\pi}{4\pi r^2}\frac{4\pi r^3 \rho}{3} = \frac{4\pi\rho}{3} r,$$

or

$$\boldsymbol{E}_r = \frac{4\pi\rho}{3}\boldsymbol{r}$$

where ***r*** is the vector from the center of the sphere to the point in question. Now suppose that ***s*** is the vector from the center of the negative sphere to the same point. Because the charge is negative, we get

$$\boldsymbol{E}_s = -\frac{4\pi\rho}{3}\boldsymbol{s}$$

So the total electric field is, using the superposition

$$\boldsymbol{E} = \boldsymbol{E}_r + \boldsymbol{E}_s = \frac{4\pi\rho}{3}(\boldsymbol{r} - \boldsymbol{s}) = \frac{4\pi\rho}{3}\boldsymbol{d}$$

For the system (sphere, radius a) with the total charge q, the charge density ρ is obtained as

$$q = \frac{4\pi R^3}{3}\rho$$

Then we have

$$E = \frac{4\pi}{3} d \frac{3q}{4\pi R^3} = \frac{qd}{R^3} = \frac{p}{R^3}$$

or

$$p = R^3 E = \alpha E$$

The polarizability is given by

$$\alpha = R^3 .$$

For the hydrogen, if we take $R = a_B$ = 0.52917721092 A, we get

$$\alpha = a_B^3 = 1.48185 \times 10^{-25} \text{ cm}^3.$$

Another method to calculate the value α is shown as follows. Here we use the formula

$$\langle r^2 \rangle = \frac{a^2}{2Z^2} n^2 [5n^2 + 1 - 3l(l+1)].$$

For $n = 1$, $Z = 1$, and $l = 0$, the radius R can be evaluated as

$$R = \sqrt{\langle r^2 \rangle} = \sqrt{3} a_B$$

for $a = a_B$. Then α is calculated as

$$\alpha = R^3 = 3\sqrt{3} a_B^3 = 5.196 a_B^3$$

Experimentally, α for hydrogen is $\alpha = 6.67 \times 10^{-25}$ cm^3 = $4.50\ a_B^3$.

APPENDIX-II Energy diagram of H_2^+ and H_2

We note that depending on the nature of textbooks, the definition of the notation is different, even the content of the physics is the same.

Energy levels of H_2^+: one-electron system

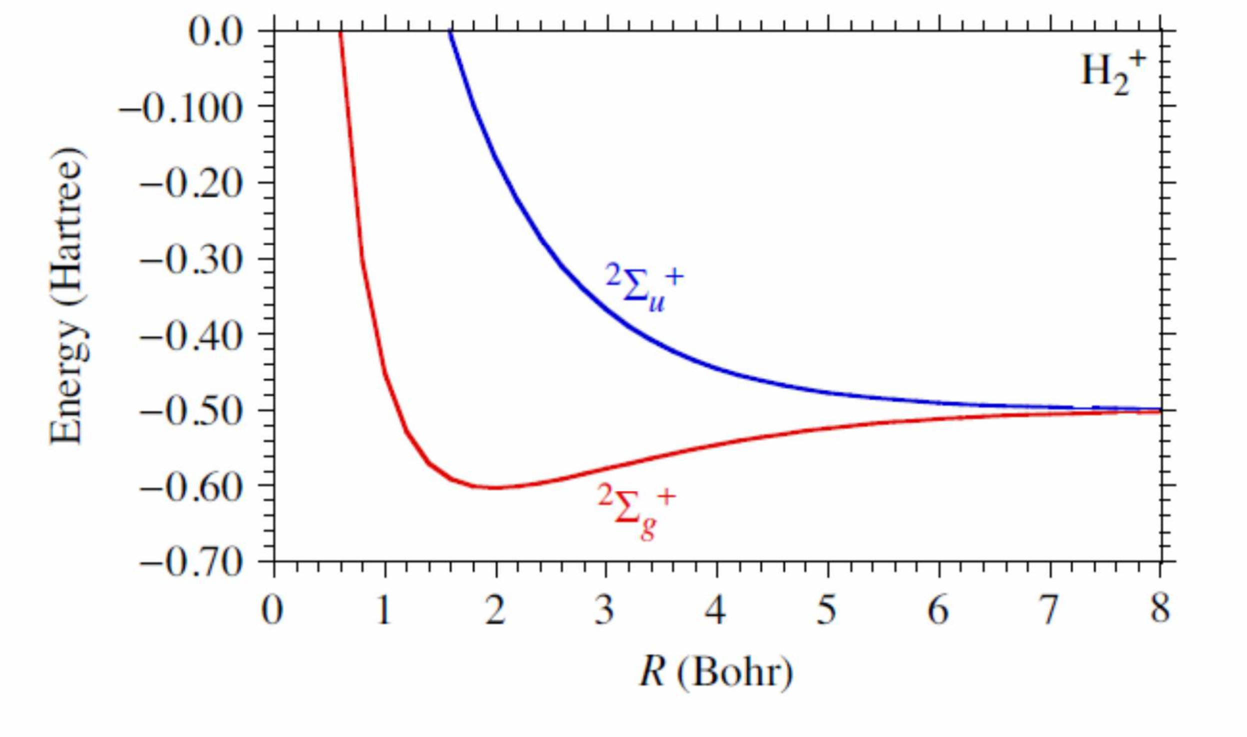


Fig. The two lowest H_2^+ potential energy curves are plotted versus the distance R.

Energy levels of H_2: two-electrons system

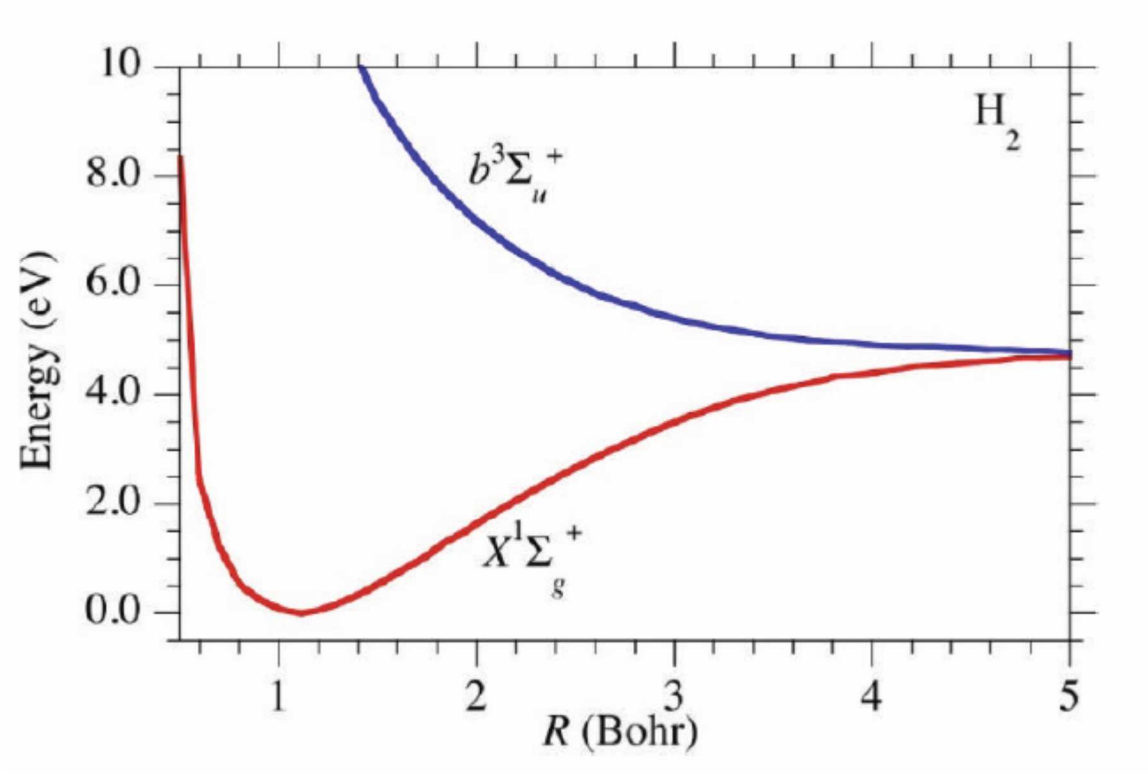


Fig. H_2 ground singlet and triplet potential curves, $(1s\sigma_g)^2 X^1\Sigma_g^+$ and $(1s\sigma_g)(1s\sigma_u)b^3\Sigma_u^+$ as a function of internuclear distance R. The singlet spin state has a spatially symmetric wave function under exchange of the two electrons, whereas the triplet spin state has a spatially antisymmetric wave function.

$(1s\sigma_g)^2 X^1\Sigma_g^+$

X:	The ground state.
1 (superscript)	Singlet
Σ	The projection of the total electronic angular momentum about the diatomic axis is zero.
g	The total two-electron wave function is even under inversion.
+	Symmetric configuration

$(1s\sigma_g)(1s\sigma_u)b^3\Sigma_u^+$

The spin is triplet (S = 1); symmetric. The spatial wave function is antisymmetric.

APPENDIX-III: Evjen method; calculation of Madelung constant

The Evjen's method requires an iterative summation of ever larger neutral cells with no accumulation of surfaces charge. This method constructs the sum so that onlyt single dipole and higher moments are used. Thus, rapid convergence is guaranteed.

The first cube surrounding the negative reference ion (denoted by red) at the point O intercepts six positive charges (1/2) on the cube faces, twelve negative charges (1/4) on the cube edges, and eight positive charges at the cube corners (1/8). The contribution to the Madelung constant from the first cube is

$$\alpha_1 = \frac{\frac{6}{2}}{1} - \frac{\frac{12}{4}}{\sqrt{2}} + \frac{\frac{8}{8}}{\sqrt{3}} = 3 - \frac{3}{\sqrt{2}} + \frac{1}{\sqrt{3}} = 1.45603$$

since

#	Fraction	p_{ij}	
6	+1/2	1	(blue)
12	-1/4	$\sqrt{2}$	(red)
8	+1/8	$\sqrt{3}$	(blue)

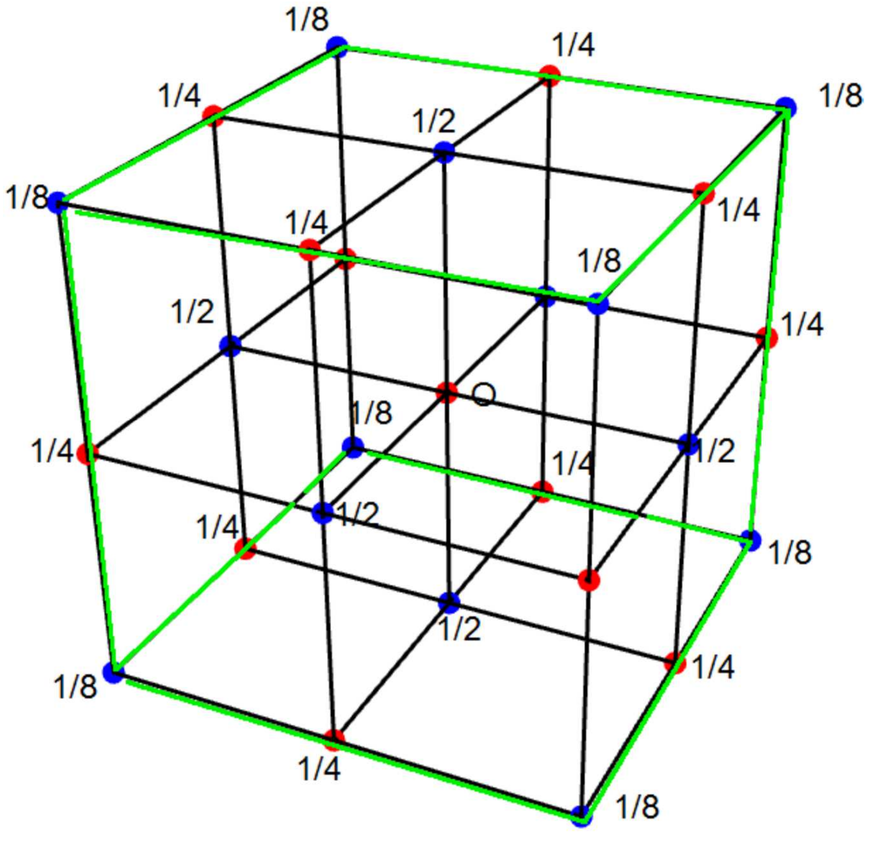


Fig. The first cube. Fractional charge assignments for the NaCl structure, arranged according to the Evjen method for calculating the Madelung constant. Face atoms carry charge 1/2; edge atoms 1/4; corner atoms 1/8.

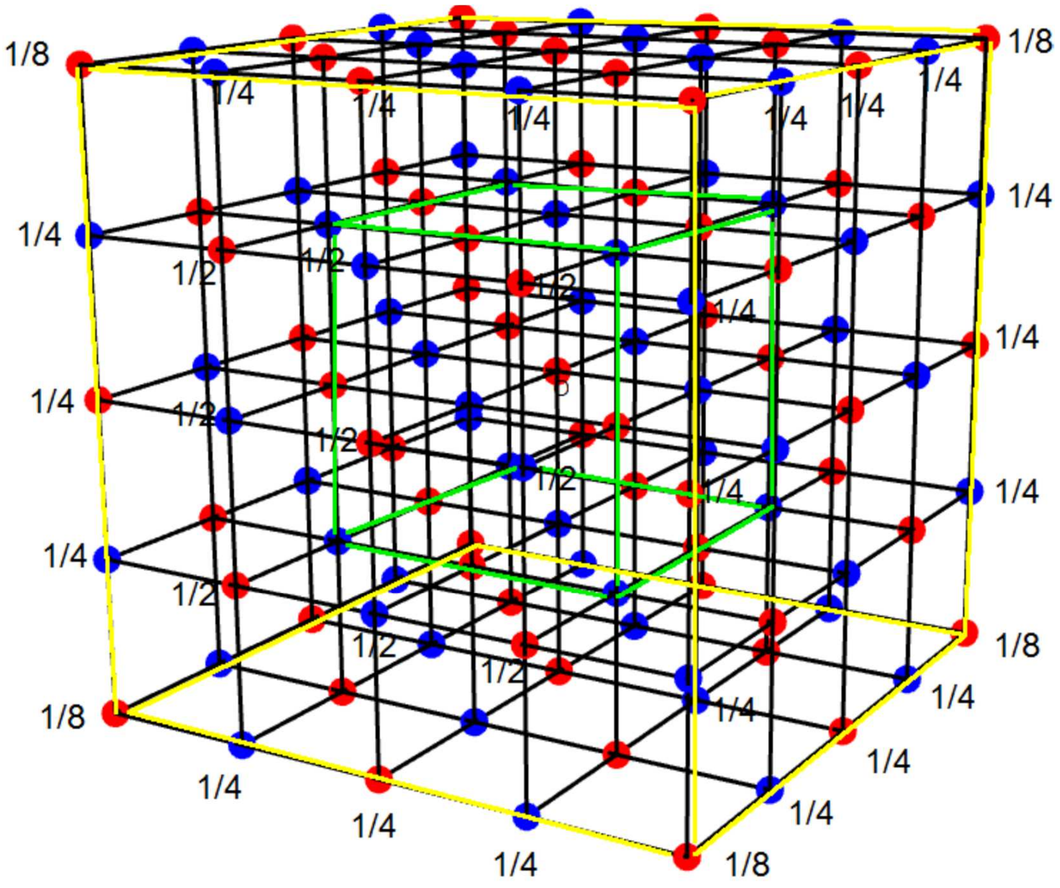


Fig. The second cube.

The contribution to the Madelung constant from the second cube:

((Inside wall))

$$\alpha_2 = \frac{\frac{6}{2}}{1} - \frac{\frac{3\times 12}{4}}{\sqrt{2}} + \frac{\frac{7\times 8}{8}}{\sqrt{3}} = 3 - \frac{9}{\sqrt{2}} + \frac{7}{\sqrt{3}} = 0.677491$$

#	Fraction	p_{ij}	
6	+1/2	1	(blue)

12	-3/4	$\sqrt{2}$	(red)
8	+7/8	$\sqrt{3}$	(blue)

((Ourside wall))

$$\alpha_3 = \frac{-\frac{6}{2}}{2} + \frac{\frac{24}{2}}{\sqrt{5}} + \frac{\frac{24}{4}}{3} - \frac{\frac{12}{4}}{2\sqrt{2}} - \frac{\frac{8}{8}}{2\sqrt{3}} - \frac{\frac{24}{2}}{\sqrt{6}} = -0.381752$$

since

#	Fraction	p_{ij}	
6	-1/2	2	(red)
24	+1/2	$\sqrt{5}$	(blue)
24	+1/4	3	(blue)
12	-1/4	$2\sqrt{2}$	(red)
8	-1/8	$2\sqrt{3}$	(red)
24	-1/2	$\sqrt{6}$	(red)

Then we have

$$\alpha = \alpha_1 + \alpha_2 + \alpha_3 = 1.74177,$$

which is very close to the exact value of the Madelung constant for NaCl;

$$\alpha = 1.74756459463318.$$

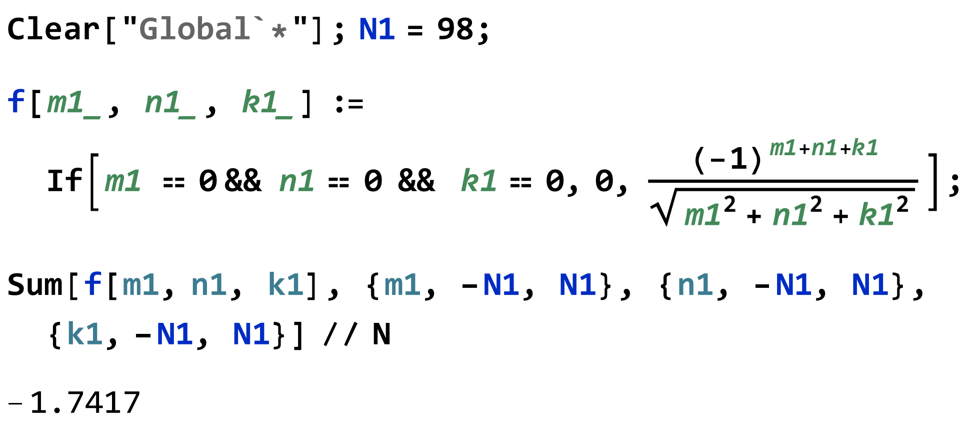
APPENDIX-IV: Mathematica for the calculation of the Madelung constanr for NaCl

(a) Direct calculation

The Madelung constant a for NaCl can be expressed by

$$\alpha = \sum_{l,m,n}^{\infty} \frac{(-1)^{l+m+n}}{\sqrt{l^2 + m^2 + n^2}}.$$

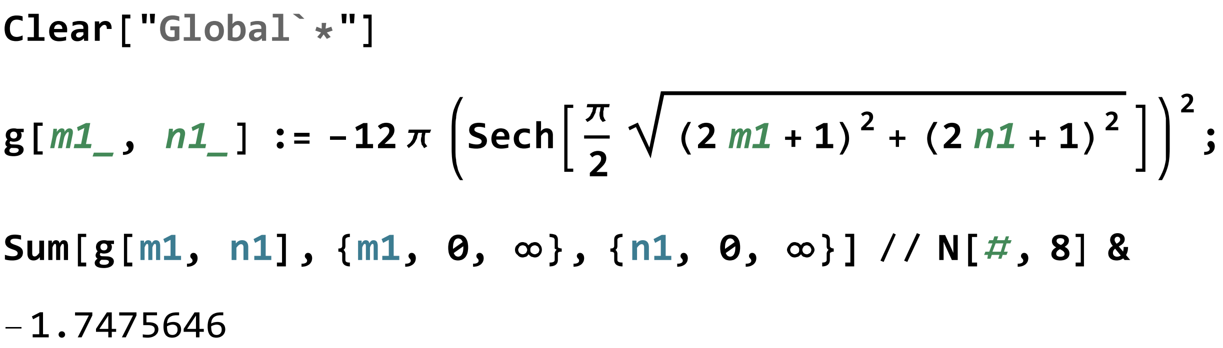
Using the Mathematica we calculate the Madelung constant as follows.



```
Clear["Global`*"]; N1 = 98;
f[m1_, n1_, k1_] :=
  If[m1 == 0 && n1 == 0 && k1 == 0, 0, (-1)^(m1+n1+k1) / Sqrt[m1^2 + n1^2 + k1^2]];
Sum[f[m1, n1, k1], {m1, -N1, N1}, {n1, -N1, N1},
  {k1, -N1, N1}] // N
-1.7417
```

(b) **Benson's formula**

$$\alpha=\sum_{l,m,n}^{\infty}\frac{(-1)^{l+m+n}}{\sqrt{l^2+m^2+n^2}}=-12\pi\sum_{\mathrm{p,q=1}}^{\infty}\operatorname{sech}^2[\frac{\pi}{2}\sqrt{(2p+1)^2+(2q+1)^2}\,]$$



```
Clear["Global`*"]
g[m1_, n1_] := -12 π (Sech[π/2 Sqrt[(2 m1 + 1)^2 + (2 n1 + 1)^2]])^2;
Sum[g[m1, n1], {m1, 0, ∞}, {n1, 0, ∞}] // N[#, 8] &
-1.7475646
```

APPENDIX-V Bulk modulus for NaCl

Compressibility and bulk modulus

$$B=-V\frac{dP}{dV}=-\frac{V}{\frac{dV}{dP}}$$

The compressibility is defined as the reciprocal of the bulk modulus. From the thermodynamics, we have the relation

$$dU=TdS-PdV\,.$$

When $dS=0$ at $T=0$ K, we get $dU=-PdV$. Thus we have

$$B = V\frac{d}{dV}\frac{dU}{dV} = V\frac{d^2U}{dV^2}$$

For NaCl, there are 4 molecules of NaCl in the conventional cubic cell with lattice constant *a*. The number of molecules in a volume *V* is

$$N = 4\frac{V}{a^3} \qquad \text{or} \qquad V = \frac{Na^3}{4}.$$

The nearest neighbor distance *R* is

$$R = \frac{a}{2}$$

Thus we have $V = 2R^3N$. Since $U = U(R)$, we use

$$\frac{dU}{dV} = \frac{dR}{dV}\frac{dU}{dR} = \frac{1}{\frac{dV}{dR}}\frac{dU}{dR} = \frac{1}{6NR^2}\frac{dU}{dR}.$$

Thus *B* can be rewritten as

$$\begin{aligned} B &= 2R^3N\frac{1}{6NR^2}\frac{d}{dR}\frac{1}{6NR^2}\frac{dU}{dR} \\ &= \frac{R}{3}\frac{d}{dR}\frac{1}{6NR^2}\frac{dU}{dR} \\ &= \frac{1}{18NR}(\frac{d^2U}{dR^2} - \frac{2}{3R}\frac{dU}{dR}) \end{aligned}$$

At the equilibrium separation $R = R_0$ and $\frac{dU}{dR} = 0$, we have

$$B = \frac{1}{18NR_0}(\frac{d^2U}{dR^2})_{R=R_0}.$$

Note that

$$U = Nz\lambda e^{-R/\rho} - \frac{N\alpha e^2}{R}.$$

$$\frac{dU}{dR} = -\frac{Nz\lambda}{\rho} e^{-R/\rho} + \frac{N\alpha e^2}{R^2}$$

$$\frac{d^2U}{dR^2} = \frac{Nz\lambda}{\rho^2} e^{-R/\rho} - \frac{2N\alpha e^2}{R^3}$$

R_0 is obtained as

$$R_0{}^2 e^{-R_0/\rho} = \frac{\rho\alpha e^2}{z\lambda}.$$

The bulk modulus *B* is

$$\begin{aligned} B &= \frac{1}{18R_0}\left(\frac{z\lambda}{\rho^2} e^{-R_0/\rho} - \frac{2\alpha e^2}{R_0{}^3}\right) \\ &= \frac{\alpha e^2}{18R_0{}^4}\left(\frac{R_0}{\alpha e^2}\frac{z\lambda}{\rho^2} R_0{}^2 e^{-R_0/\rho} - 2\right) \\ &= \frac{\alpha e^2}{18R_0{}^4}\left(\frac{R_0}{\rho} - 2\right) \end{aligned}$$

For NaCl, B = 2.40 x 10^{11} dyne/cm^2 = 2.4 x 10^{10} Pa = 24.0 GPa

((**Note**))

GPa=10^9 N/m^2. N = 10^5 dyne, Pa = 10 dyne/cm^2.