

Quantum Chemistry

Lecture 12

Variational principle

NC State University

Variational energy of a diatomic

We can apply the variational principle to the average energy:

$$E = \frac{\int \Psi H \Psi d\tau}{\int \Psi \Psi d\tau}$$

In this case we can define our basis as

$$\Psi = c_1 \phi_1 + c_2 \phi_2$$

where the variational parameters are the coefficients c_1 and c_2 . Thus, we will use this definition of a basis to obtain an expression for the energy and subsequently find the minimum energy using the conditions,

$$\frac{\partial E}{\partial c_1} = 0, \quad \frac{\partial E}{\partial c_2} = 0$$

Variational energy of a diatomic

The numerator is

$$\int \Psi H \Psi d\tau = \int (c_1 \phi_1^* + c_2 \phi_2^*) H (c_1 \phi_1 + c_2 \phi_2) d\tau$$

Which has four terms

$$c_1^2 \int \phi_1^* H \phi_1 d\tau + c_2^2 \int \phi_2^* H \phi_2 d\tau + c_1 c_2 \int \phi_1^* H \phi_2 d\tau + c_2 c_1 \int \phi_2^* H \phi_1 d\tau$$

We can use the following notation for the energies to simplify the presentation,

$$H_{ij} = \int \phi_i^* H \phi_j d\tau$$

The terms H_{ii} are the energies of an electron on nucleus i and the terms H_{ij} are resonance integrals that represent the contribution to the energy from an electron shared between nuclei i and j .

Variational energy of a diatomic

In an analogous manner we can express the denominator as,

$$\int \Psi \Psi d\tau = \int (c_1 \phi_1^* + c_2 \phi_2^*)(c_1 \phi_1 + c_2 \phi_2) d\tau$$

Which has four terms

$$c_1^2 \int \phi_1^* \phi_1 d\tau + c_2^2 \int \phi_2^* \phi_2 d\tau + c_1 c_2 \int \phi_1^* \phi_2 d\tau + c_2 c_1 \int \phi_2^* \phi_1 d\tau$$

We can use the following notation to simplify the presentation,

$$S_{ij} = \int \phi_i^* \phi_j d\tau$$

where the integrals S_{ij} are overlap integrals. The integrals $S_{ii} = 1$ since the atomic wavefunctions are normalized.

Variational energy of a diatomic

Using these definitions and substituting into the equation for the energy we find.

$$E = \frac{H_{11}c_1^2 + H_{22}c_2^2 + 2c_1c_2H_{12}}{c_1^2 + c_2^2 + 2c_1c_2S_{12}}$$

We now apply the variational principle by taking the derivatives with respect coefficients (the coefficients are the variational parameters). We can rewrite the equation as:

$$E(c_1^2 + c_2^2 + 2c_1c_2S_{12}) = H_{11}c_1^2 + H_{22}c_2^2 + 2c_1c_2H_{12}$$

Then take the derivative. Using the product rule we find:

$$\frac{\partial E}{\partial c_1}(c_1^2 + c_2^2 + 2c_1c_2S_{12}) + E(2c_1 + 2c_2S_{12}) = 2H_{11}c_1 + 2c_2H_{12}$$

Variational energy of a diatomic

Since the derivative of E with respect to c_1 is zero we have

$$E(2c_1 + 2c_2S_{12}) = 2H_{11}c_1 + 2c_2H_{12}$$

Collecting terms, this equation can be written as

$$(H_{11} - E)c_1 + (H_{12} - ES_{12})c_2 = 0$$

Using a similar procedure for c_2 we find:

$$(H_{12} - ES_{12})c_1 + (H_{22} - E)c_2 = 0$$

$$\det \begin{bmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - E \end{bmatrix} = 0$$

$$(H_{11} - E)(H_{22} - E) - (H_{12} - ES_{12})^2 = 0$$

Variational energy of a diatomic

$$E^2 - (H_{11} + H_{22})E + H_{11}H_{22} - E^2S_{12}^2 + 2ES_{12}H_{12} - H_{12}^2 = 0$$

$$E^2(1 - S_{12}^2) - (H_{11} + H_{22} - 2S_{12}H_{12})E + H_{11}H_{22} - H_{12}^2 = 0$$

$$E = \frac{(H_{11} + H_{22} - 2S_{12}H_{12}) \pm \sqrt{(H_{11} + H_{22} - 2S_{12}H_{12})^2 - 4(1 - S_{12}^2)(H_{11}H_{22} - H_{12}^2)}}{2(1 - S_{12}^2)}$$

This general case cannot be factored further. However, if we assume that $H_{11} = H_{22}$, this implies that $c_1 = c_2$. Then we can make the following identifications,

$$H_{11} = H_{22} = \alpha, H_{12} = \beta$$

The determinant becomes:

$$\det \begin{bmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{bmatrix} = 0$$

Variational energy of a diatomic

$$(\alpha - E)^2 - (\beta - ES)^2 = 0$$

$$E = \frac{(2\alpha - 2S\beta) \pm \sqrt{(2\alpha - 2S\beta)^2 - 4(1 - S^2)(\alpha^2 - \beta^2)}}{2(1 - S^2)}$$

The factor of 2 in both numerator and denominator cancel. Inside the square root we have:

$$(\alpha^2 - 2S\alpha\beta + S^2\beta^2) - (\alpha^2 - \beta^2) + S^2(\alpha^2 - \beta^2) = (\beta - S\alpha)^2$$

which simplifies to

$$E = \frac{(\alpha - S\beta) \pm (\beta - S\alpha)}{(1 - S^2)}$$

After simplification the energies for the two levels are:

$$E_{\pm} = \frac{\alpha \pm \beta}{1 \pm S}$$

Wave functions of a diatomic

The corresponding wave functions are: σ_g^+ and σ_u^+

These solutions justify the treatment of homonuclear diatomics. We can form linear combinations of the various orbitals (1s, 2s, 2p_{x,y}, 2p_z etc.) and that for each of them we will construct bonding (+) and anti-bonding (-) MO for the diatomic.

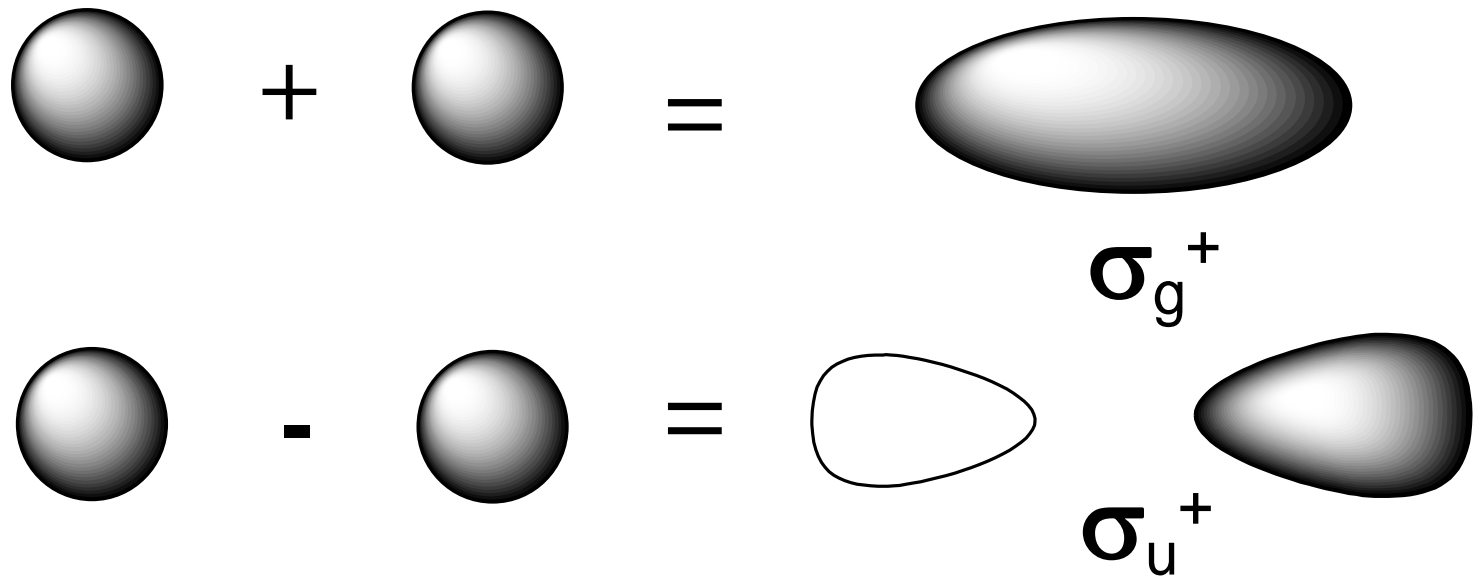
For two s orbitals the irreducible representations are

$$\psi_{\pm} = \frac{1}{\sqrt{1 \pm S}} (\phi_1 \pm \phi_2)$$

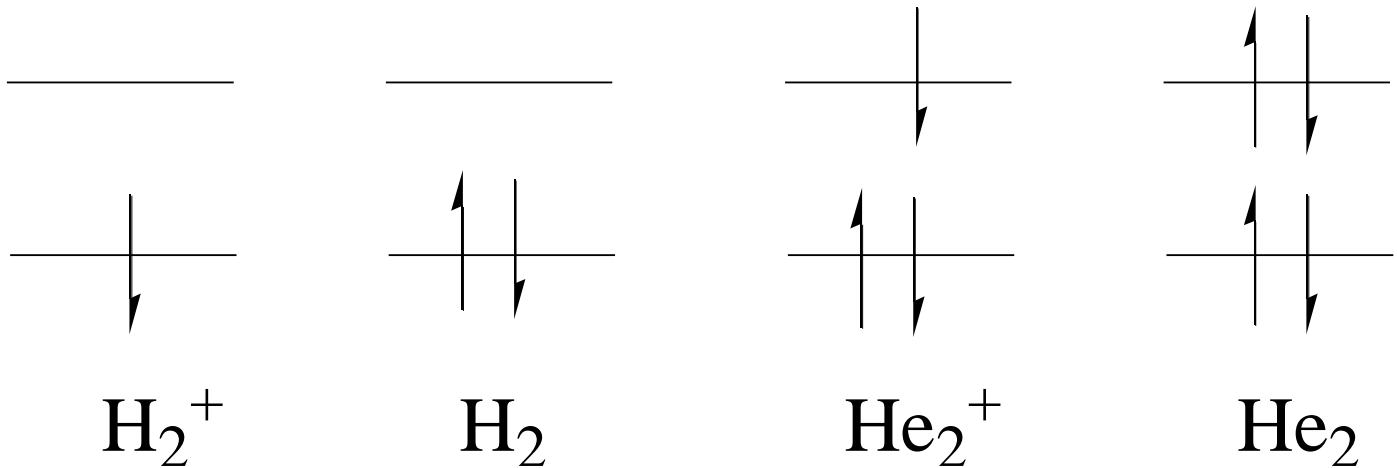
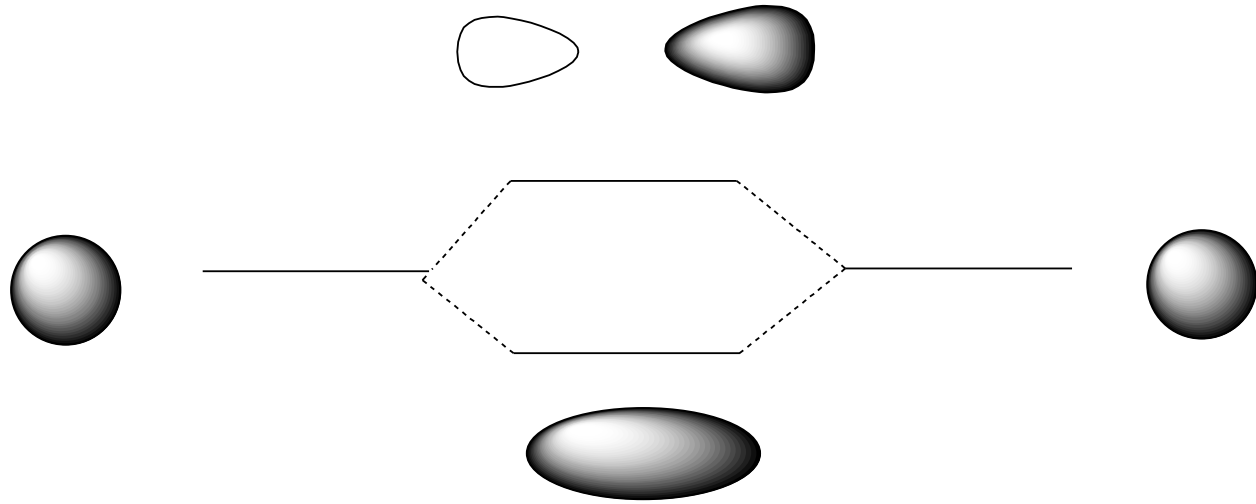
corresponding to the bonding and anti-bonding linear combinations, respectively.

$$\sigma_g^+ = \frac{1}{\sqrt{2 + 2S}} (\psi_{ns,a} + \psi_{ns,b}) \quad \sigma_g^- = \frac{1}{\sqrt{2 - 2S}} (\psi_{ns,a} - \psi_{ns,b})$$

Wave functions of a diatomic



Wave functions of a diatomic



Wave functions of a diatomic

To continue the procedure for the remaining diatomic molecules in the first row of the periodic table, we can consider the analogous population $2s$ orbital. However, this cannot be done without also included the 3 $2p$ orbitals, $2p_x$, $2p_y$ and $2p_z$. Thus, we can consider the remaining diatomic molecules in the first row of the periodic table to arise from population of the eight possible linear combinations.

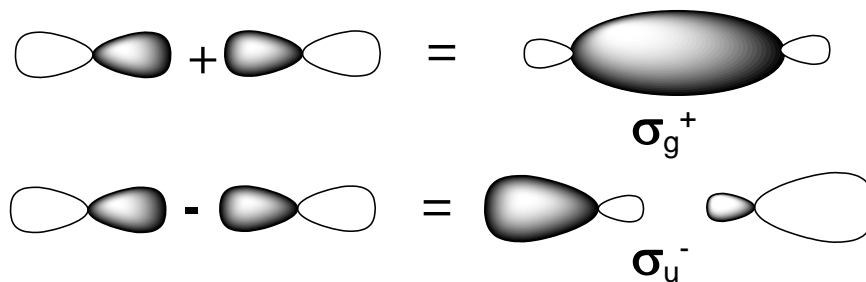
In addition to the $2s$ orbitals we can construct bonding and anti-bonding linear combinations from the $2p$ orbitals using a similar approach. We must distinguish between the $2p_z$, which lie along the internuclear axis and the $2p_{x,y}$, which are perpendicular to that axis. The $2p_z$ orbitals for the following linear combinations,

In addition to the 2s orbitals we can construct bonding and anti-bonding linear combinations from the 2p orbitals using a similar approach. We must distinguish between the $2p_z$, which lie along the internuclear axis and the $2p_{x,y}$, which are perpendicular to that axis. The $2p_z$ orbitals for the following linear combinations,

$$\sigma_g^+ = \frac{1}{\sqrt{2 + 2S}} (\psi_{np_z,a} + \psi_{np_z,b})$$

$$\sigma_u^+ = \frac{1}{\sqrt{2 - 2S}} (\psi_{np_z,a} - \psi_{np_z,b})$$

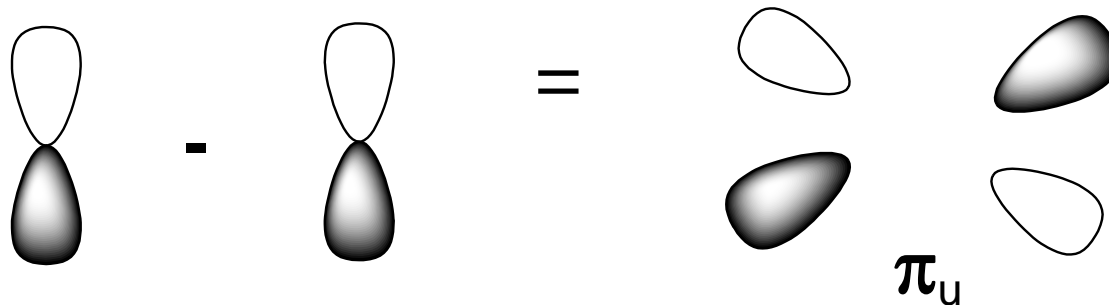
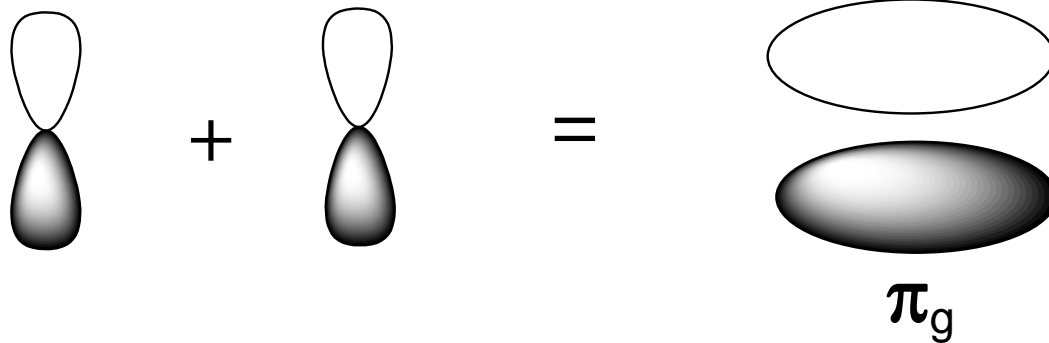
These orbitals have the appearance:

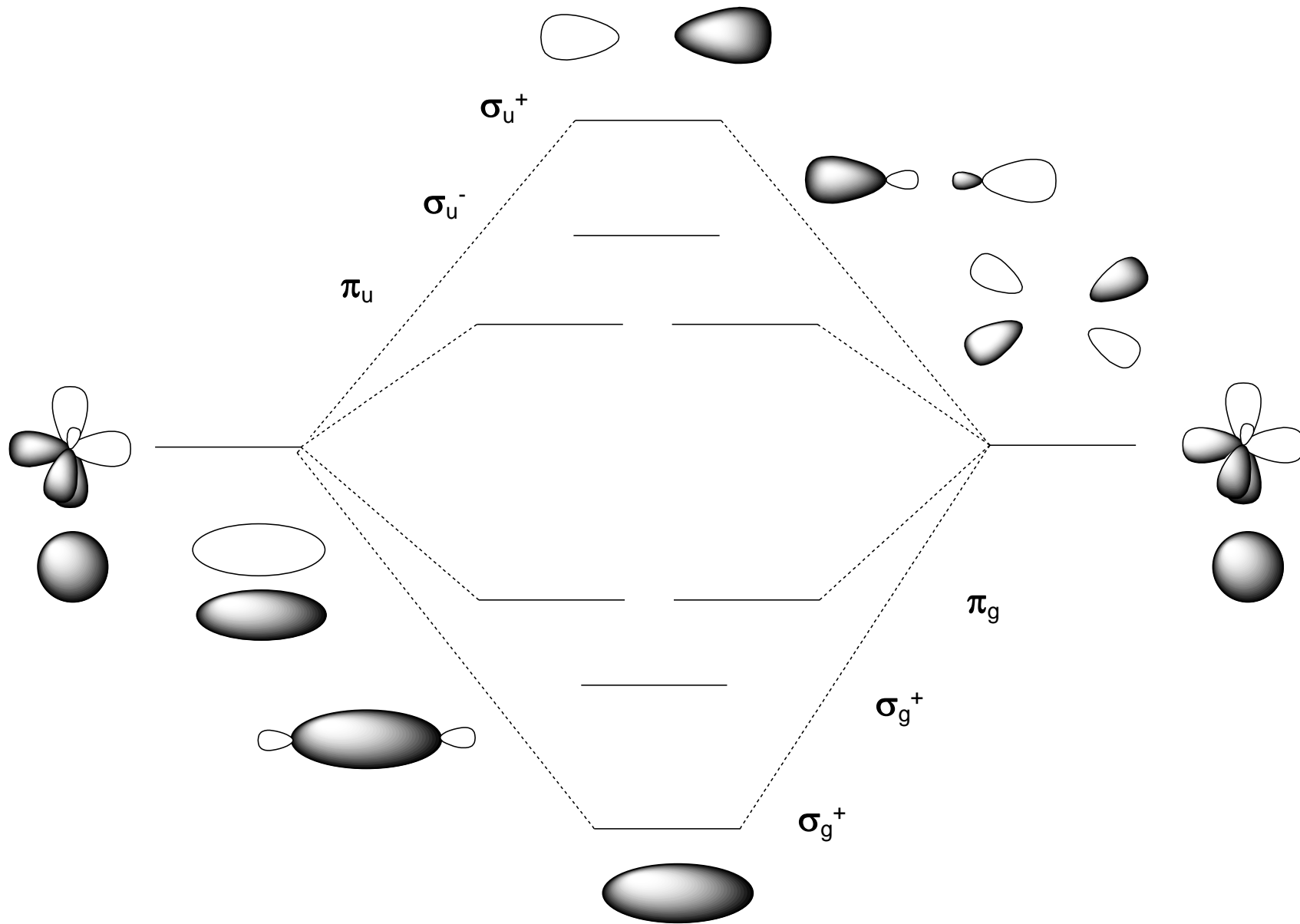


π -bonding linear combinations

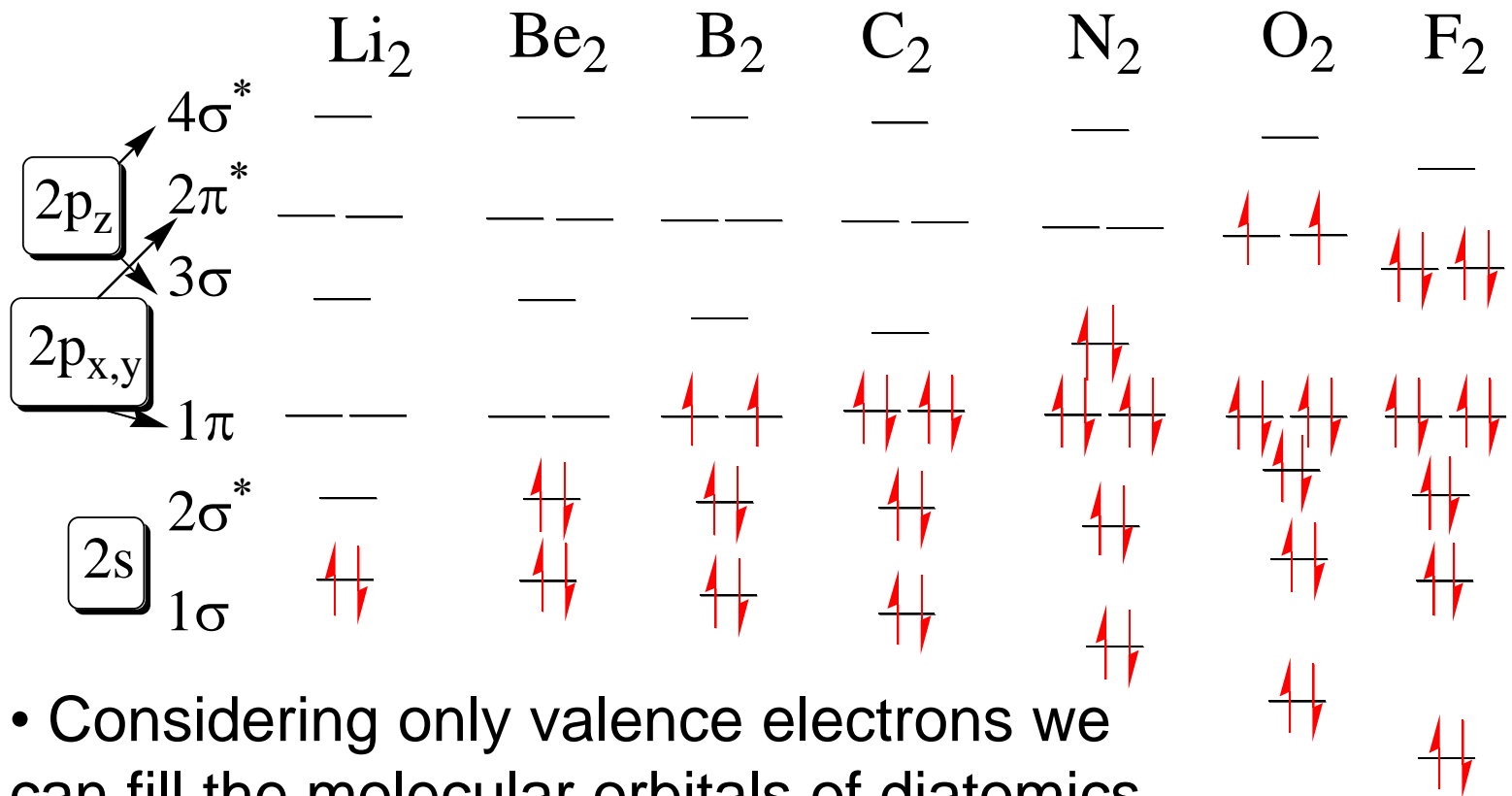
The $p_{x,y}$ orbitals form a degenerate set and transform as π_g and π_u

$$\pi_g = \frac{1}{\sqrt{2+2S}} (\psi_{np_{x,y},a} + \psi_{np_{x,y},b}) \quad \pi_u = \frac{1}{\sqrt{2-2S}} (\psi_{np_{x,y},a} - \psi_{np_{x,y},b})$$





Application to diatomic molecules



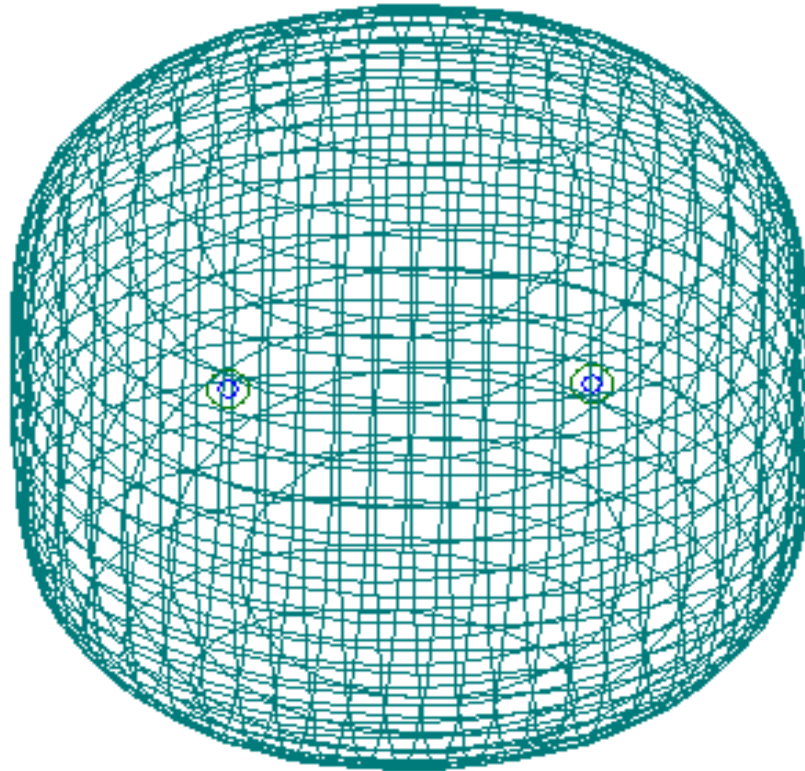
- Considering only valence electrons we can fill the molecular orbitals of diatomics.
- Linear combinations of 2s, 2p_z give s orbitals.
- Linear combinations of 2p_{x,y} give p orbitals.
- The relative energy ordering depends on the number of electrons in occupied orbitals.

Nitrogen Molecular Orbitals

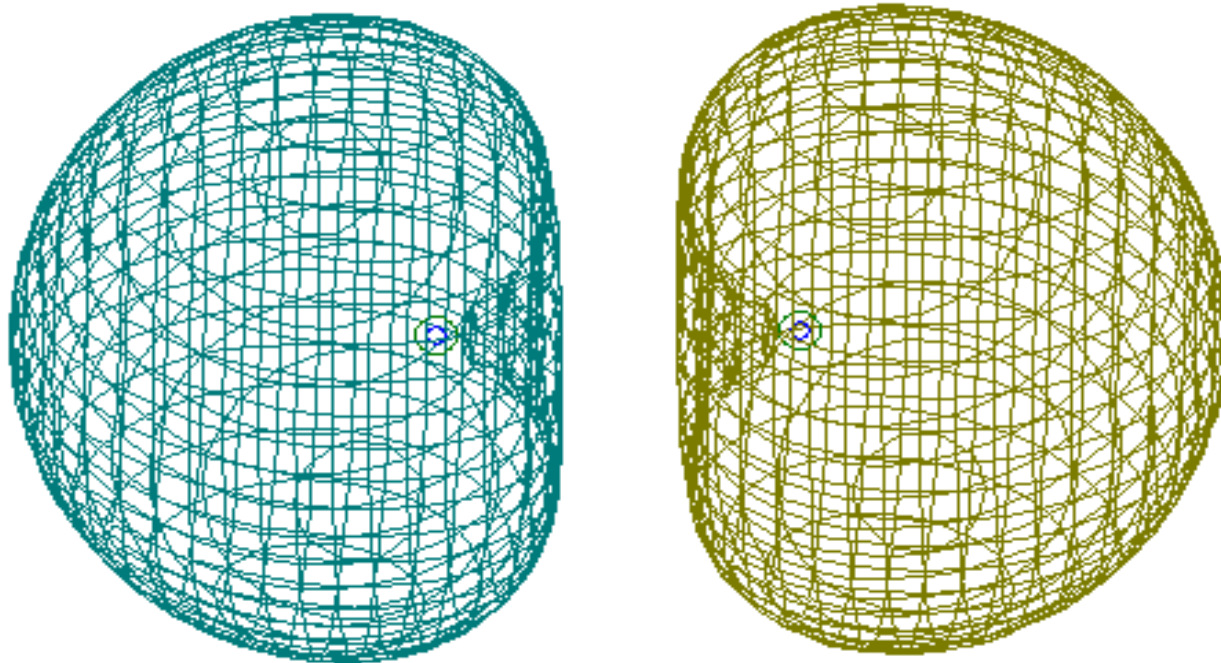
Example of a Homonuclear Diatomic

- Isosurfaces represent $\phi^*\phi$ of orbital showing 90% of total probability.
- The spatial wavefunction is an LCAO.
- Core electrons are not included.
- There are five electrons for each N atom.

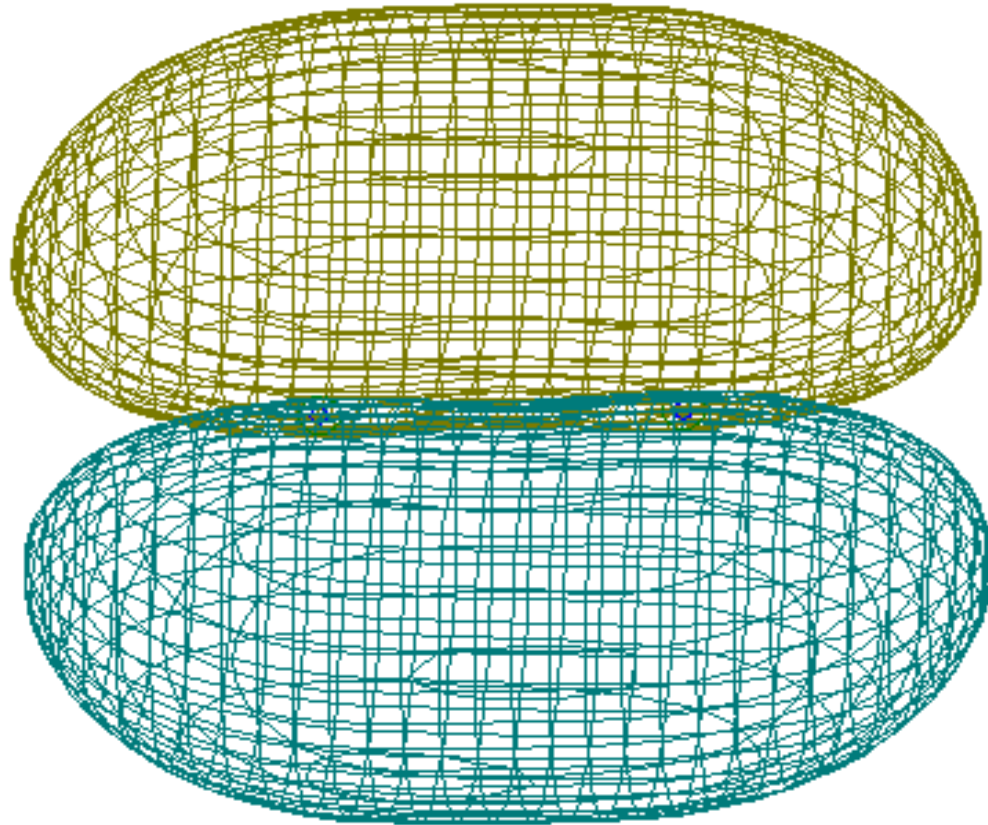
Dinitrogen 1σ MO



N_2 $2\sigma^*$ MO

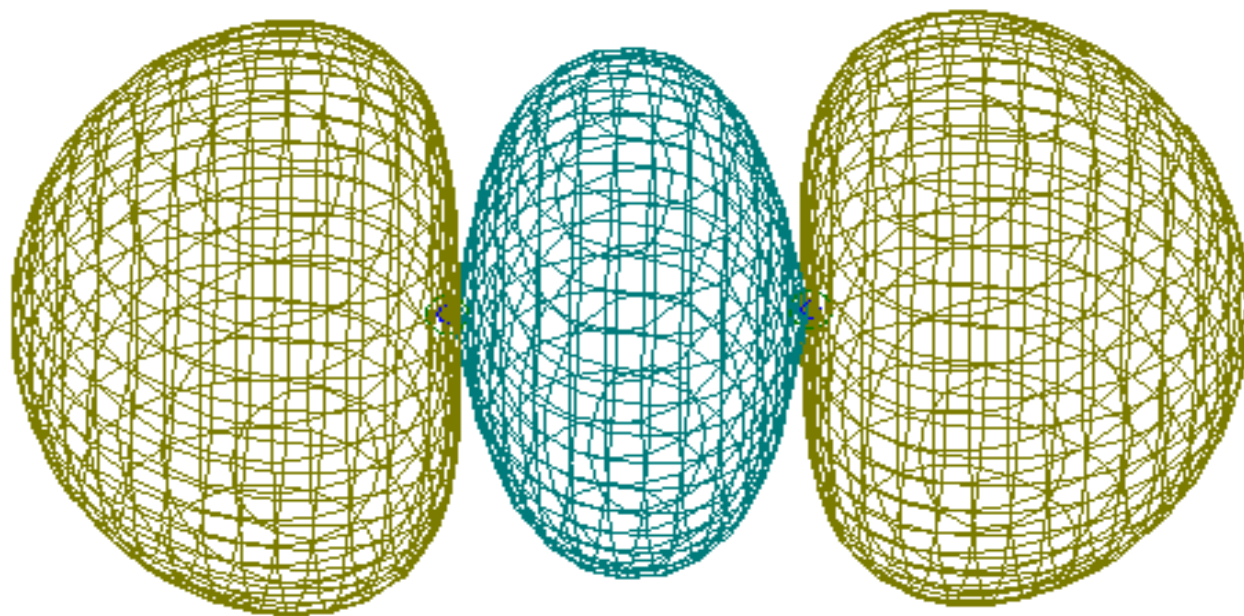


N_2 1π MO

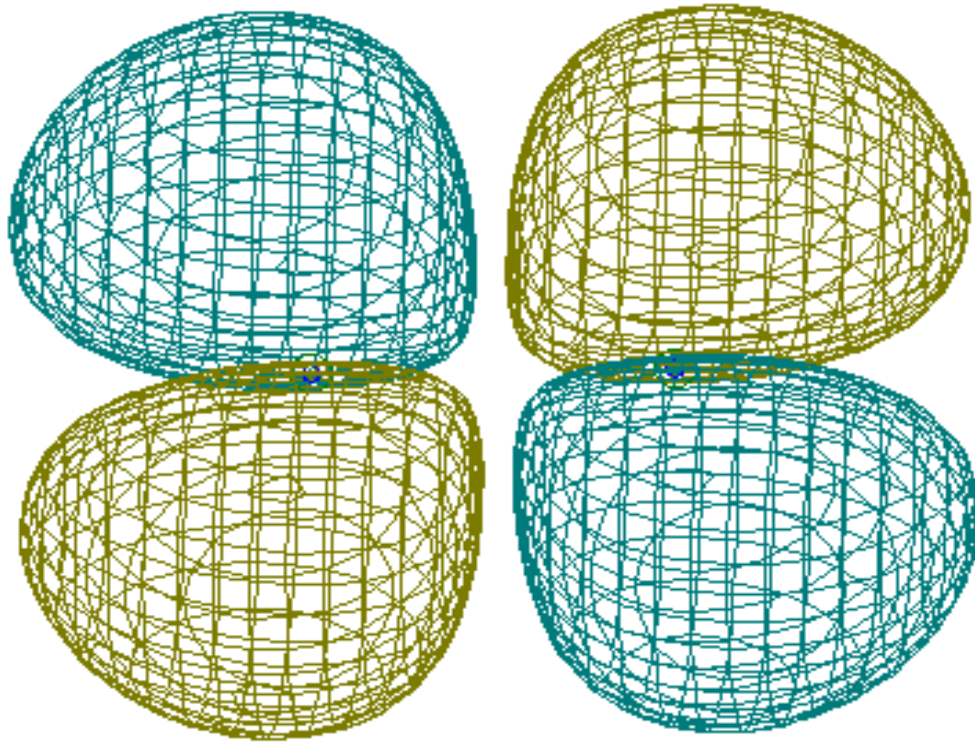


This is a doubly degenerate orbital.
Only one of the two is shown.

N_2 3σ MO

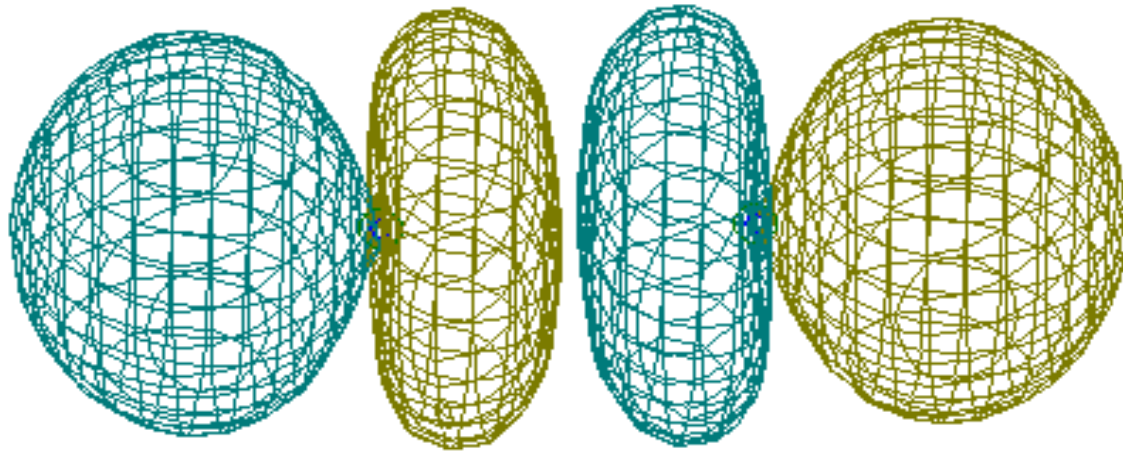


N_2 $2\pi^*$ MO



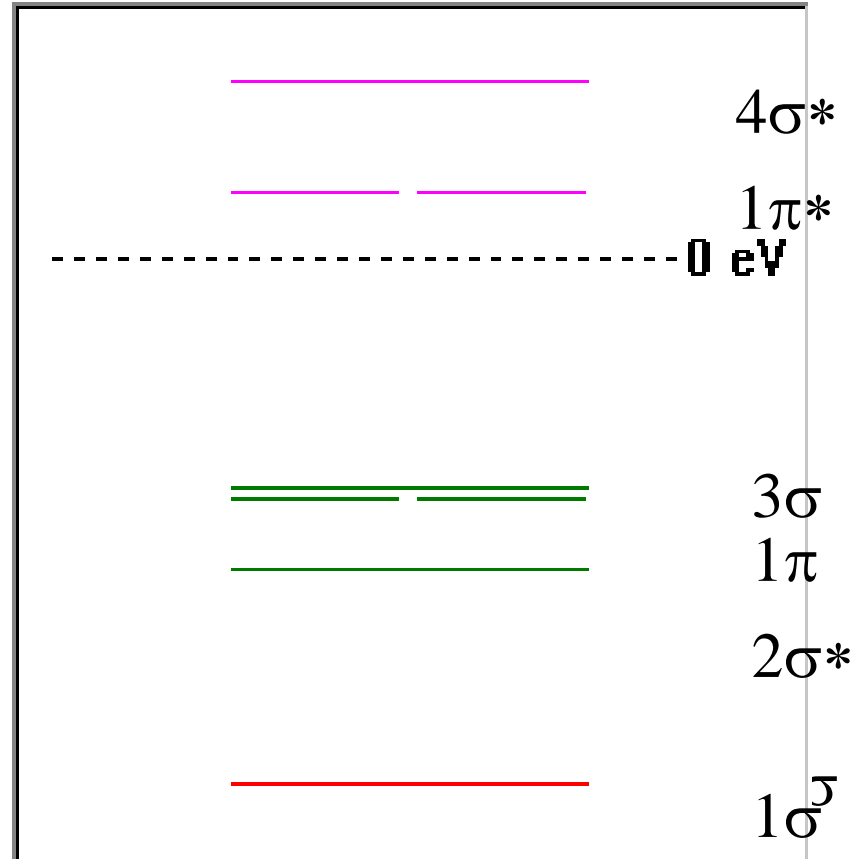
This is a doubly degenerate orbital.
Only one of the two is shown.

N_2 $4\sigma^*$ MO



Energy level diagram for N₂

- Negative energies represent bonding interactions (< 0 eV)
- For N₂ all there are ten electrons so all orbitals are filled through 3s
- Only valence orbitals are shown



Ground State Molecular Properties

- Bond length (structure).
- Vibrational frequency:
 - Calculated at stationary point.
 - Depends on accuracy of second derivative matrix with respect to nuclear displacement.
- Dipole moment (clearly zero for N_2).

Koopman's theorem

We can think of the individual orbitals as representing the energy required to pull an electron off of the molecule out of an occupied orbital or add one to an unoccupied orbital. Such an approach is a frozen electron approximation. This means that we assume that none of the remaining electrons will respond to the electron removal or addition. The formal statement of this approach is Koopman's theorem.

The ionization potential and electron affinity can be obtained from the energy of removal or addition of an electron to a molecular orbital at the single-determinant level.

Heteronuclear diatomics

We can further exemplify the method for the heteronuclear diatomic, for which $c_1 \neq c_2$.

In this case we can use the following identifications:

$$H_{11} = \alpha_1, H_{22} = \alpha_2, H_{12} = \beta$$

The determinant becomes:

$$\det \begin{bmatrix} \alpha_1 - E & \beta - ES \\ \beta - ES & \alpha_2 - E \end{bmatrix} = 0$$

$$(\alpha_1 - E)(\alpha_2 - E) - (\beta - ES)^2 = 0$$

Heteronuclear diatomic

To express the solutions in compact form we introduce the trigonometric representation:

$$\tan(2\theta) = \frac{2\beta}{\alpha_1 - \alpha_2}$$

In this case the energies are:

$$E_+ \approx \alpha_1 - \frac{\tan^2(2\theta)}{4}$$

$$E_- \approx \alpha_2 + \frac{\tan^2(2\theta)}{4}$$

The wave functions are:

$$\psi_- = -\sin(\theta)\phi_1 + \cos(\theta)\phi_2$$

$$\psi_+ = \cos(\theta)\phi_1 + \sin(\theta)\phi_2$$

Heteronuclear diatomic

These approximate models for formation of bonding interactions can be applied to appropriate valence atomic orbitals on each center. We can approximate the energy of the electron each center α_i by the ionization potential of the electron in that orbital. This is an application of Koopman's theorem. Koopman's theorem states that the energy of an orbital is approximately equal to the ionization energy of an electron in that MO. This is a convenient approximation since it permits the use of X-ray photoelectron spectroscopy to measure the electron energies of both valence and core MOs.

Heteronuclear diatomic

The resonance energy that appears in the above equations can be estimated using semi-empirical theories, which are described in the next chapter. For example, we can consider bonding in HF. From the previous section we have seen that bonding in H_2 and F_2 can be considered to arise from two 1s and two 2p_z orbitals, respectively. Thus, bonding in HF arises from the interaction of a 1s and a 2p_z orbital. We have the following initial values,

Heteronuclear diatomic

Thus,

$$\alpha_{\text{H}} = E_{\text{H},1s} = -13.6 \text{ eV} , \alpha_{\text{F}} = E_{\text{F},2p_z} = -18.6 \text{ eV} , \beta_{\text{HF}} = 2.0 \text{ eV} ,$$

$$\tan(2\theta) = \frac{\beta_{\text{HF}}}{\alpha_{\text{H}} - \alpha_{\text{F}}} = -0.8$$

and

$$\theta = -19^\circ$$

. The energies are

$$E_+ = -19.3 \text{ eV}$$

$$E_- = -12.9 \text{ eV}$$

The net stabilization in the bonding orbital is 0.7 eV. The wave functions are

$$\psi_{\text{bonding}} = 0.33\psi_{\text{H},1s} + 0.94\phi_{\text{F},2p_z}$$

Potential energy surfaces

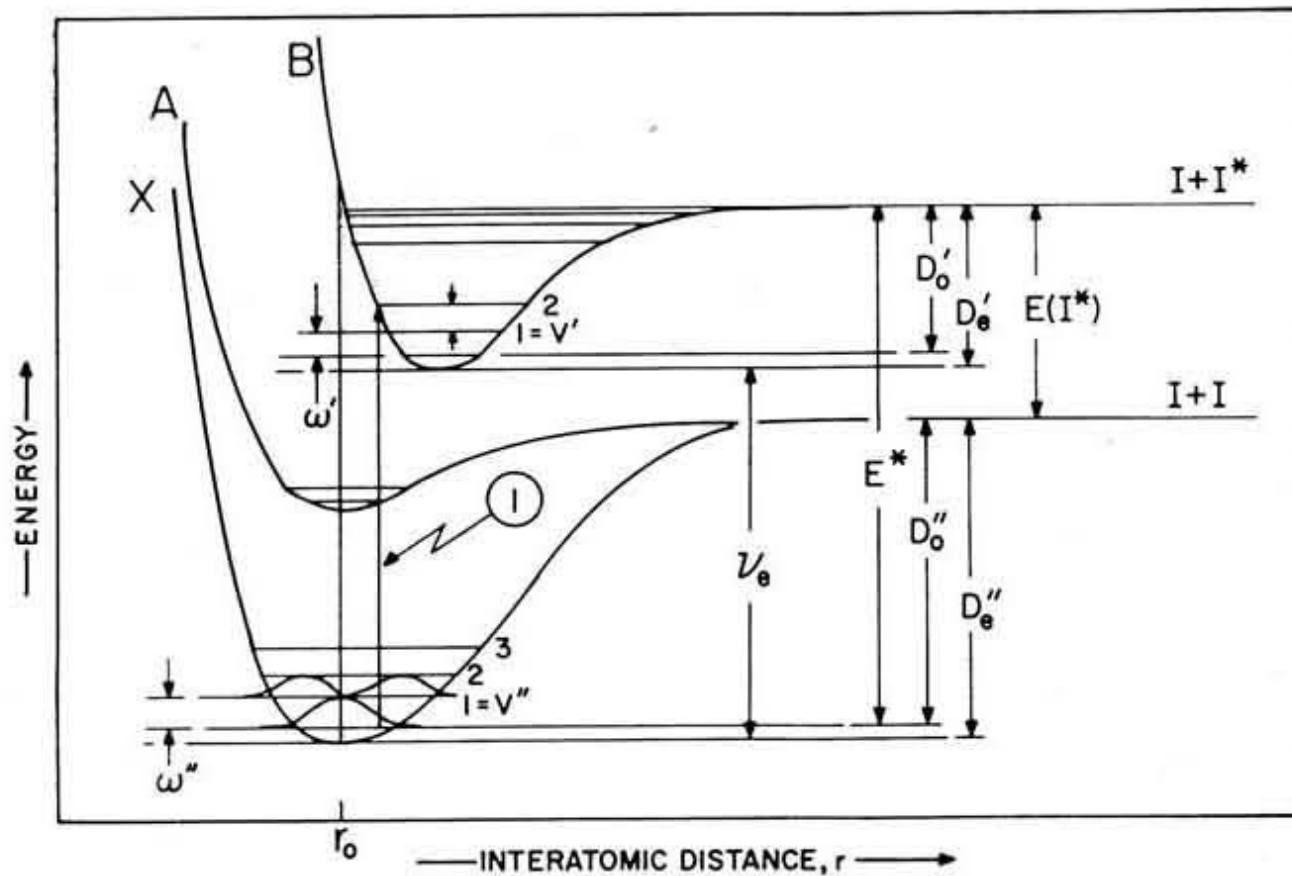


Figure 1. Representative potential energy curves for diatomic homonuclear halogens.

Spectroscopic transitions

- Energy is sum of electronic, vibrational and rotational.

$$E(n, v, J) = E^{elec}(n) + E_n^{vib}(v) + E_{n,v}^{rot}(J)$$

- The observed transitions are expressed as

$$\hbar\omega = T'_e + G'(v') - T''_e + G''(v'')$$

- T_e is the electronic energy and $G(v)$ is the vibrational energy (see next page)
- The vibrational energies include anharmonicity.

$$G(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2$$

Terminology for diatomic spectroscopy

- In Herzberg and in the literature on diatomic molecules one prime (‘) represents the excited state and two primes (‘’) represents the ground state.
- T_e designates the electronic energy at the equilibrium bond length. $T_e'' = 0$ for the ground state by definition.
- ν_e designates the transition energy $T_e' - T_e''$.
- $G(v)$ represents the vibrational energy above T_e .
- ω_e represents the vibrational frequency
- $\omega_e x_e$ represents the anharmonicity constant.

Birge-Sponer Extrapolation

