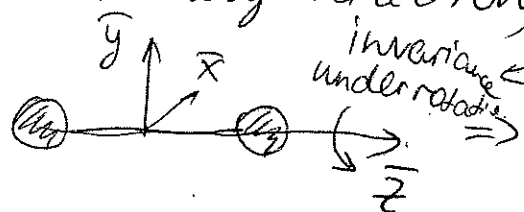


Molecular structure: symmetries

Recall: (H) -atom $\Rightarrow [H, \vec{L}^2] = 0, [H, L_z] = 0$
 N -electron atom without fine s hyperfine structure

Y_e^m
 \Leftarrow Total orbital momentum \vec{L} is conserved
 (z - arbitrary direction) $\Rightarrow L, M_L$ conserved

Now:  $[L_z, H_e] = 0$, but $[H_e, L_x] \neq 0$
 \Downarrow $T_e + V$ \leftarrow Lecture # 21

diatomic molecule

$$L_z \varphi_s = \hbar M_L \varphi_s$$

electronic eigenfunction of a diatomic molecule

$0, \pm 1, \pm 2$

Introduce

$$\Lambda = |M_L| = 0, 1, 2, \dots$$

absolute value of the projection of the total electronic orbital angular momentum on the internuclear axis

$$\varphi_s \approx \frac{1}{\sqrt{2\pi}} e^{\pm i\Lambda\varphi}$$

(analog of s, p, d, f... in atoms) \Downarrow spectroscopic terms

$$\Lambda = 0 \quad 1 \quad 2 \quad 3$$

$$\Sigma \quad \Pi \quad \Delta \quad \varphi$$

or individual electrons $\Rightarrow |m_l| = \lambda$

$$\lambda = 0 \quad 1 \quad 2 \quad 3$$

$$\sigma \quad \pi \quad \delta \quad \varphi \dots$$

(analog of s, p, d, f...)

Other symmetries:

(2)

Invariance with respect to $\bar{y} \rightarrow -\bar{y}$ (reflection in one operator performs reflection $\bar{x}\bar{z}$ -plane)

$$[A_{\bar{y}}, H_e] = 0$$

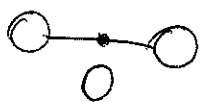
$$\{A_{\bar{y}}, L_{\bar{z}}\} = 0$$

$\Rightarrow \Lambda \neq 0$ states (Π, Δ, Φ, \dots) are doubly-degenerate

Σ states $\Rightarrow \Sigma^{\pm}$
 ↑
 charges sign
 ← wave function unchanged upon reflection in $\bar{x}\bar{z}$

Homonuclear diatomic molecule (H_2, N_2, O_2, \dots)

\Rightarrow



symmetry with respect to O

Odd \Rightarrow ungerade

\Downarrow

Σ_u, Π_u, \dots

H_e is invariant

under $\vec{r}_i \rightarrow -\vec{r}_i$

↑
 center of symmetry

or

even \Rightarrow gerade
 states

\Rightarrow

Σ_g, Π_g, \dots

multiplicity of the term

$2S+1 \Rightarrow$

Example of notations \Rightarrow

$X^1\Sigma^+$

← homonuclear molecule

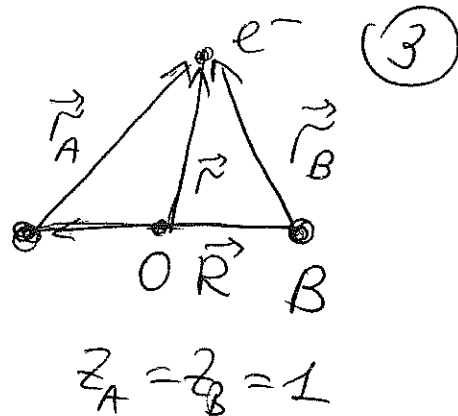
for homonuclear

↑
 ground state

excited states: A, B, C, ...

$X^1\Sigma_g^+$

Example Hydrogen ion H_2^+
molecular



in a.u.

$$H_e = -\frac{1}{2} \nabla_{\vec{r}}^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

Need to solve:

$$H_e \Psi_s = E_s \Psi_s(\vec{R}; \vec{r})$$

Note: This is the only problem that can be solved exactly using Born-Oppenheimer approach.

But: choose approximate method

pp. 495-496 of B&J

linear combination of atomic orbitals (LCAO)

Ground state $\Rightarrow \Psi_{1s} \Rightarrow$ but: $\Psi_{1s}(r_A)$ or $\Psi_{1s}(r_B)$?

at $R \rightarrow \infty$ need to consider even (gerade) and odd (ungerade) combinations

$$\Psi_{g,u}(\vec{R}; \vec{r}) = \frac{1}{\sqrt{2}} (\Psi_{1s}(r_A) \pm \Psi_{1s}(r_B))$$

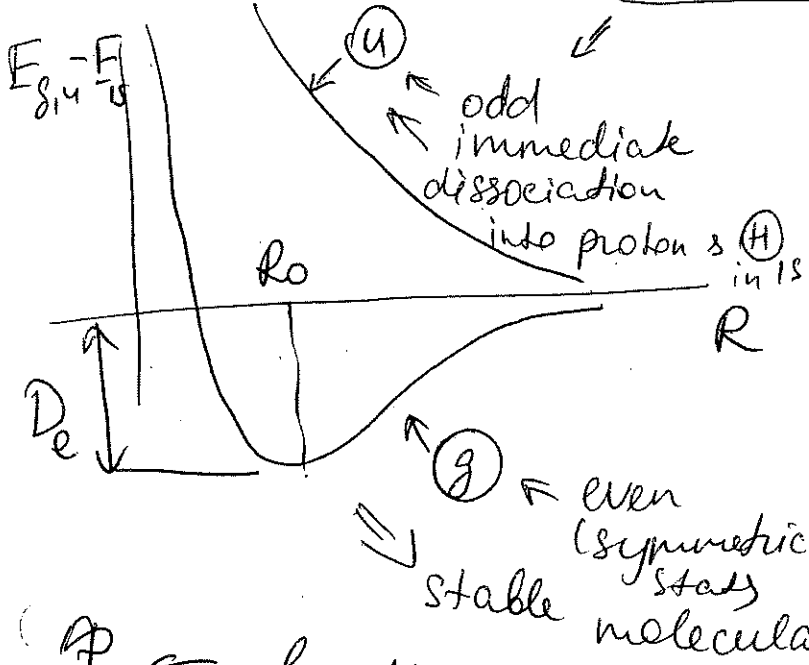
\nwarrow σ_g
 \nwarrow σ_u

But what about smaller R 's? \Rightarrow use $\Psi_{g,u}$ as trial functions

$$E_{g,u}(R) = \frac{\int \Psi_{g,u}^* H_e \Psi_{g,u} d\vec{r}}{\int |\Psi_{g,u}|^2 d\vec{r}}$$

Work through pp. 492-493 and Appendix 10 (4)

$$E_{g,u}(R) = E_{1s} + \frac{1}{R} \frac{(1+R)e^{-2R} \pm (1 - \frac{2R^2}{3})e^{-R}}{1 \pm (1+R + \frac{R^2}{3})e^{-R}}$$



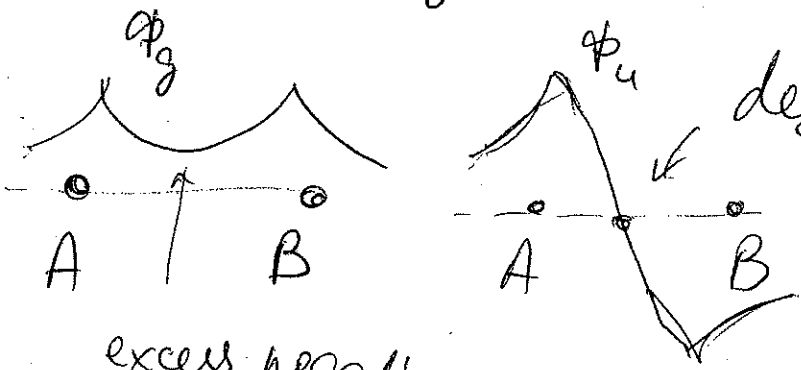
Exact result $R_0 = 2.49 a.u. = 1.32 \text{ \AA}$
 $R_0 = 2 a.u. = 1 \text{ \AA}$
 LCAO: $R_0 = 2.49 a.u. = 1.32 \text{ \AA}$

$D_e = 1.77 \text{ eV} \leftarrow \text{LCAO}$
 $2.79 \text{ eV} \leftarrow \text{exact}$

$\Phi_g \leftarrow$ bonding molecular orbital $\Rightarrow \sigma_g 1s$

$\Phi_u \leftarrow$ antibonding orbital $\Rightarrow \sigma_u^* 1s$

Can improve approximation by setting $Z \rightarrow Z^*$ and find Z^* using variational method



deficiency of the negative charge \Rightarrow antibonding

excess negative charge
 $\rho_g = -e |\Phi_g|^2 \Rightarrow$ binding (bonding)

Note: H_2 - molecule:
 experiment $R_0 \sim 0.8 \text{ \AA}$ \leftarrow LCAO
 $D_e \sim 2.68 \text{ eV}$
 Exact: $R_0 = 0.74 \text{ \AA}; D_e = 4.75 \text{ eV}$