Šred. j-na koja prikazuje kretanje e^- u potencijalnom polju jezgara a i b ima oblik:

$$\hat{A}\,\bar{\Phi} = E\,\bar{\Phi}$$

ili: $$\nabla^2 \Phi + \frac{2m}{\hbar^2}\left[E + \frac{e^2}{r_a} + \frac{e^2}{r_b} - \frac{e^2}{r_{ab}}\right]\Phi = 0 \qquad \left[\frac{1}{4\pi\varepsilon_0} = 1\right]$$

m – masa elektrona; ∇^2 se odnosi na koordinate elektrona.

Mi ćemo sada da aproksimativno odredimo Φ koristeći method of the linear combination of atomic orbitals (LCAO).
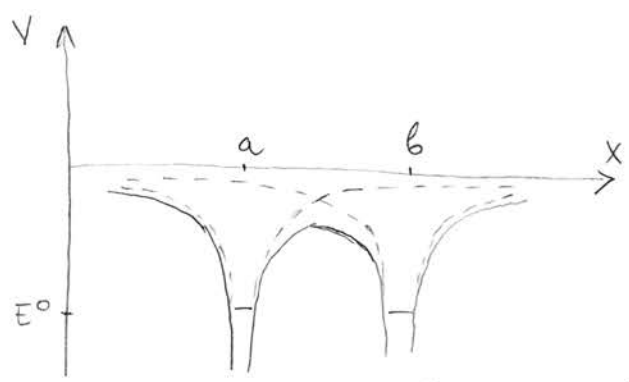
Potenc. energija koja deluje na e^- usled privlačnih sila od a i b. Isprekidana kriva pokazuje energiju e^- u polju nukleusa a ili nukleusa b posebno. Puna kriva je ukupna potenc. energija. Vezivna energija e^- u polju jednog nukleusa je E^o.
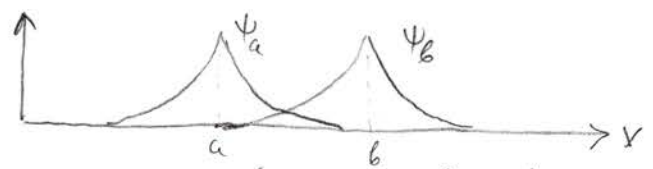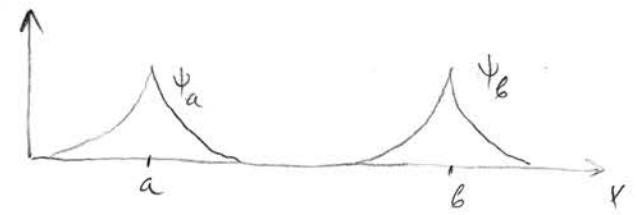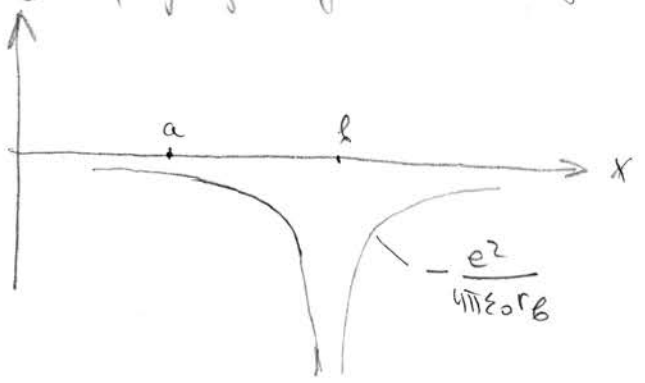
Gornji grafik: Tal. f-ja ψ_a elektrona koji se kreće u polju nukleusa a i odgovarajuća t.f. ψ_b za e^- susednog nukleusa.

Donji grafik: Ako se rastojanje između a i b smanjuje to počinju t. f-je da se prepokrivaju.

obično crtamo
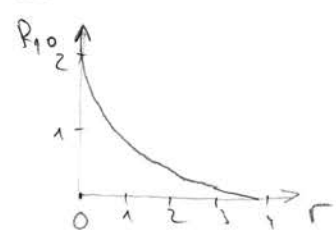
Dakle, pišemo:

$$\Phi = c_a \psi_a + c_b \psi_b$$

$$\psi_a = \frac{1}{\sqrt{\pi a^3}} e^{-r_a/a} \quad ; \quad \psi_b = \frac{1}{\sqrt{\pi a^3}} e^{-r_b/a}$$

Odredimo prvo koeficijente c_a i c_b.

$$\hat{H} \psi_a c_a + \hat{H} \psi_b c_b = E \psi_a c_a + E \psi_b c_b$$

Izmnožimo prvo sa leve strane sa ψ_a^* pa integralimo, a onda sa ψ_b^* pa opet integralimo:

$$\left(\int \psi_a^* \hat{H} \psi_a \, d\tau - E \int \psi_a^* \psi_a \, d\tau \right) c_a + \left(\int \psi_a^* \hat{H} \psi_b \, d\tau - E \int \psi_a^* \psi_b \, d\tau \right) c_b = 0 \qquad (1)$$

$$\left(\int \psi_b^* \hat{H} \psi_a \, d\tau - E \int \psi_b^* \psi_a \, d\tau \right) c_a + \left(\int \psi_b^* \hat{H} \psi_b \, d\tau - E \int \psi_b^* \psi_b \, d\tau \right) c_b = 0 \qquad (2)$$

Uvedimo: $\int \psi_a^* \hat{H} \psi_a \, d\tau = H_{aa}$; $\int \psi_b^* \hat{H} \psi_b \, d\tau = H_{bb}$ } Molecular Coulomb integral

$\int \psi_a^* \hat{H} \psi_b \, d\tau = H_{ab}$; $\int \psi_b^* \hat{H} \psi_a \, d\tau = H_{ba}$ } Resonance integral.

$\int \psi_a^* \psi_a \, d\tau = \int \psi_b^* \psi_b \, d\tau = 1$; $\int \psi_a^* \psi_b \, d\tau = S_{ab} ; \int \psi_b^* \psi_a \, d\tau = S_{ba}$

onda:

$$\begin{vmatrix} H_{aa} - E & H_{ab} - S_{ab} E \\ H_{ba} - S_{ba} E & H_{bb} - E \end{vmatrix} = 0$$

zbog simetrije $S_{ab} = S_{ba} = S$

a zbog ermitivnosti $\hat{H}$ biće: $H_{ab} = H_{ba}$; $H_{aa} = H_{bb}$

$$\Rightarrow \quad \begin{vmatrix} H_{aa} - E & H_{ab} - SE \\ H_{ab} - SE & H_{aa} - E \end{vmatrix} = 0$$

$$(H_{aa} - E)^2 = (H_{ab} - SE)^2 \quad \text{imamo 2 rešenja}$$

$$H_{aa}^2 - 2E H_{aa} + E^2 = H_{ab}^2 - 2 H_{ab} SE + S^2 E^2$$

$$E^2 (1 - S^2) - 2E (H_{aa} - H_{ab} S) + H_{aa}^2 - H_{ab}^2$$

$$E_{1,2} = \frac{2(H_{aa} - H_{ab} S) \pm \sqrt{(H_{aa}^2 - 2 H_{aa} H_{ab} S + H_{ab}^2 S^2) 4 - 4(1 - S^2)(H_{aa}^2 - H_{ab}^2)}}{2(1 - S^2)}$$

$$= \frac{2(H_{aa} - H_{ab} S) \pm \sqrt{4 H_{aa}^2 - 8 H_{aa} H_{ab} S + 4 H_{ab}^2 S^2 - 4 H_{aa}^2 + 4 H_{ab}^2 + 4 S^2 H_{aa}^2 - 4 S^2 H_{ab}^2}}{2(1 - S^2)} = \frac{2(H_{aa} - H_{ab} S) \pm \sqrt{4(S H_{aa} - H_{ab})^2}}{2(1 - S^2)}$$

$$E_{1,2} = \frac{2(H_{aa} - H_{ab}S) \pm 2(SH_{aa} - H_{ab})}{2(1-S^2)} = \frac{H_{aa} - H_{ab}S \pm SH_{aa} \mp H_{ab}}{1-S^2}$$

$$E_{1,2} = \frac{H_{aa}(1 \pm S) \mp H_{ab}(1 \pm S)}{1-S^2} = \frac{(1 \pm S)(H_{aa} \mp H_{ab})}{(1+S)(1-S)} =$$

$$\longrightarrow \frac{H_{aa} - H_{ab}}{1-S} \equiv E_A$$

$$\longrightarrow \frac{H_{aa} + H_{ab}}{1+S} \equiv E_S$$

Zamenom E_S u (1) tj. u $(H_{aa} - E)c_a + (H_{ab} - SE)c_b = 0$

dobija se: $\left(H_{aa} - \frac{H_{aa} + H_{ab}}{1+S}\right)c_a + \left(H_{ab} - S\frac{H_{aa} + H_{ab}}{1+S}\right)c_b = 0$

$$\frac{(1+S)H_{aa} - H_{aa} - H_{ab}}{1+S}c_a + \left(\frac{H_{ab}(1+S) - SH_{aa} - SH_{ab}}{1+S}\right)c_b = 0$$

$$(SH_{aa} - H_{ab})c_a + (H_{ab} - SH_{aa})c_b = 0 \quad \Rightarrow \quad \boxed{c_a = c_b}$$

Zamenom E_A u (2) tj. u $(H_{ba} - ES)c_a + (H_{bb} - E)c_b = 0$

$$\left(H_{ba} - \frac{H_{aa} - H_{ab}}{1-S}S\right)c_a + \left(H_{bb} - \frac{H_{aa} - H_{ab}}{1-S}\right)c_b = 0$$

$$[H_{ab}(1-S) - H_{aa}S + H_{ab}S]c_a + [\underset{(=H_{aa})}{H_{bb}}(1-S) - H_{aa} + H_{ab}]c_b = 0$$

$$(H_{ab} - H_{aa}S)c_a + (-H_{aa}S + H_{ab})c_b = 0$$

$$(H_{ab} - H_{aa}S)(c_a + c_b) = 0$$

$\Rightarrow$ $\overline{\text{Imamo}}$ dva rešenja $\quad c_a = c_b \quad$ i $\quad c_a = -c_b$

Ove konstante se određuju iz uslova normiranja

$$\int \Phi^* \Phi d\tau = \int (c_a \psi_a^* + c_b \psi_b^*)(c_a \psi_a + c_b \psi_b) d\tau = 1$$

$$\Rightarrow c_a^2 + 2c_a c_b S + c_b^2 = 1$$

Za slučaj $c_a = c_b \Rightarrow \qquad c_a = c_b = \frac{1}{\sqrt{2(1+S)}}$

i $\qquad\qquad c_a = -c_b = \frac{1}{\sqrt{2(1-S)}}$

Dakle, simetrična f-ja je:

$$\Phi_S = \frac{1}{\sqrt{2(1+S)}}\left(\psi_a + \psi_b\right)$$
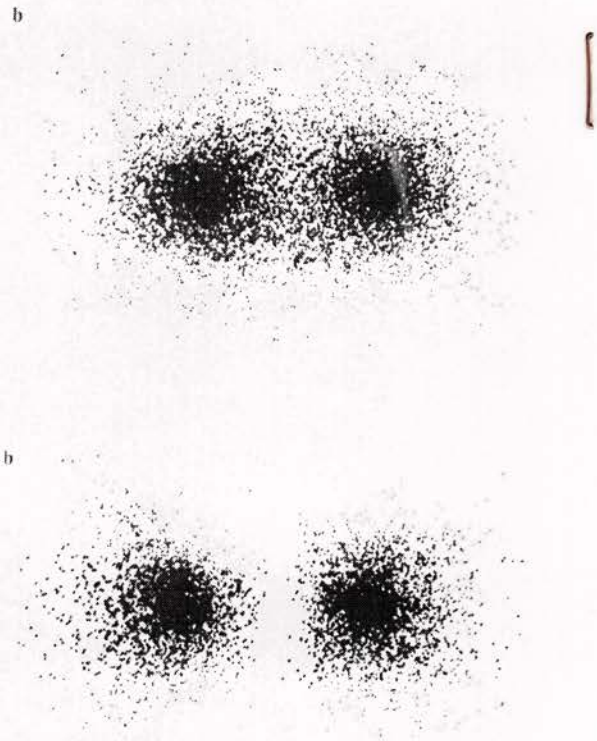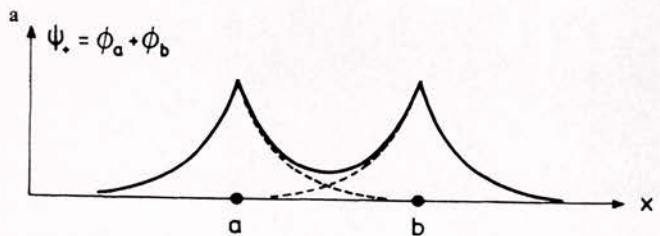
$$\Phi_A = \frac{1}{\sqrt{2(1-S)}}\left(\psi_a - \psi_b\right)$$

a

$\psi_+ = \phi_a + \phi_b$

a   b   x

b

Fig. 24.6. a) The symmetric wavefunction ψ_+ is formed by superposing the wave-functions ϕ_a and ϕ_b. Because of the overlap between ϕ_a and ϕ_b, the occupation probability for ψ_+ between the two nuclei is increased. **b)** Illustration of the density distribution of the electron in the ψ_+ state
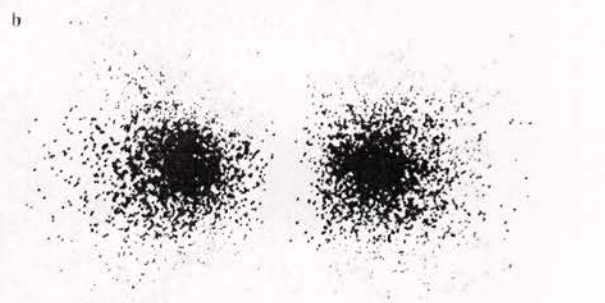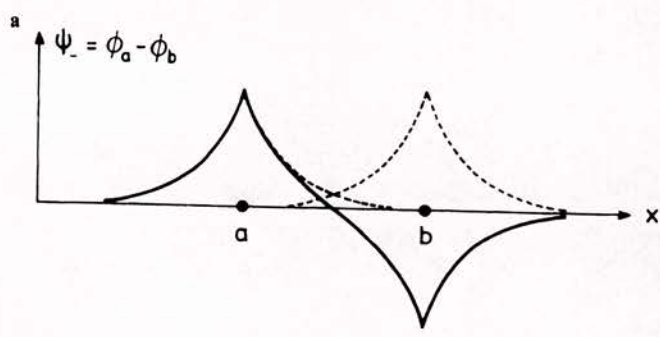
a

$\psi_- = \phi_a - \phi_b$

a   b   x

b

Fig. 24.7. a) The antisymmetric wavefunction ψ_- is formed by taking the difference of ϕ_a and ϕ_b. The occupation probability is clearly zero in the plane of symmetry between the two nuclei. **b)** Illustration of the density distribution of the electron in the hydrogen-molecule ion in the case of the antisymmetric wavefunction ψ_-

ϕ_a^2

a   b   x

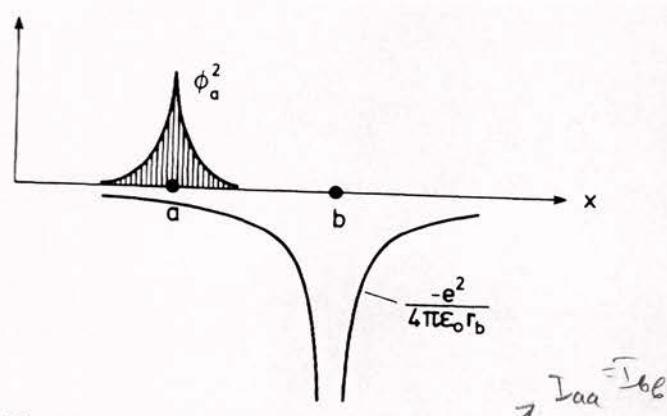$-\dfrac{e^2}{4\pi\varepsilon_0 r_b}$

$I_{aa} = I_{bb}$

Fig. 24.4. Intuitive explanation of the integral (24.8). This integral represents the Coulomb interaction energy of an electron density cloud with the probability density distribution ϕ_a^2 in the Coulomb field of the nucleus. The density distribution is shown as a shaded area, while the full curve gives the potential energy of a point charge in the Coulomb field of nucleus b. To calculate the integral, at each point in space the value of ϕ_a^2 must be multiplied with the corresponding value of $-e^2/(4\pi\varepsilon_0 r_b)$ and the products must be added (integrated) over the entire volume
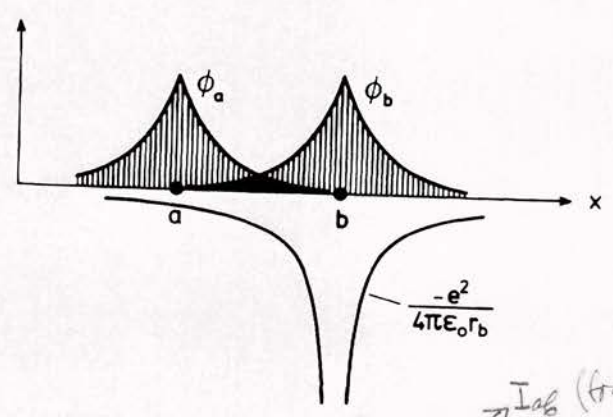
ϕ_a ϕ_b

a   b   x

$-\dfrac{e^2}{4\pi\varepsilon_0 r_b}$

I_{ab}

Fig. 24.5. Intuitive explanation of the integral (24.9). The three functions ϕ_a, ϕ_b, and $-e^2/(4\pi\varepsilon_0 r_b)$ which occur in the integral are plotted. Since the product of these three functions occurs, nonvanishing contributions are only possible when the wavefunctions ϕ_a and ϕ_b overlap, as is indicated by the heavily shaded area. The integral is obtained by multiplying the functional values of ϕ_a, ϕ_b, and $-e^2/(4\pi\varepsilon_0 r_b)$ at each point in space and adding up over the whole volume
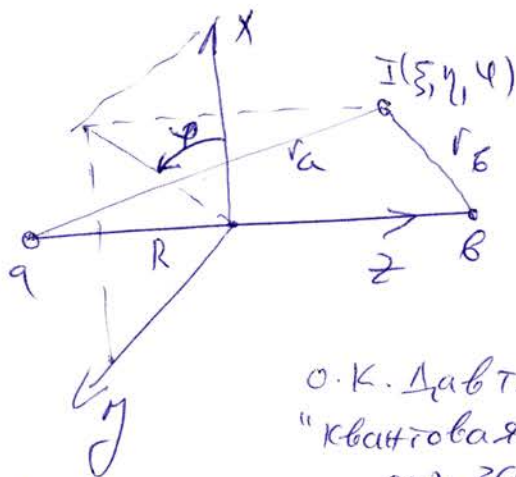
Eliptične koordinate:

Uzme li se koordinatni početak negde u nekoj tački na r_{ab} i z-osa duž $r_{ab}(=R)$ onda se tri eliptične koordinate tačke u kojoj se nalazi elektron (ξ, η, φ) definišu ovako:

$$\xi = \frac{r_a + r_b}{R} \; ; \quad \eta = \frac{r_a - r_b}{R}, \quad \varphi$$

$$\xi \in [1, \infty] \; ; \quad \eta \in [-1, +1] \; ; \quad \varphi \in [0, 2\pi].$$

φ - ugao obrtanja oko prave koja spaja jezgra a i b

$I(\xi, \eta, \varphi)$

Inverzne rel. su:

$$r_a = \frac{R}{2}(\xi + \eta) \; ; \quad r_b = \frac{R}{2}(\xi - \eta)$$

$$d\tau = \frac{R^3}{8}(\xi^2 - \eta^2) \, d\xi \, d\eta \, d\varphi = dx \, dy \, dz$$

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" Квантовая хими:
стр. 365:

H_{aa} i H_{ab} integrali

$$H_{aa} = \int \psi_a^* \hat{H} \psi_a \, d\tau = \int \psi_a^* \left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r_a} - \frac{e^2}{r_b} + \frac{e^2}{r_{ab}} \right] \psi_a \, d\tau$$

$$= E_{1s} \int \psi_a^* \psi_a \, d\tau - e^2 \int \psi_a^* \frac{1}{r_b} \psi_a \, d\tau + e^2 \int \psi_a^* \frac{1}{(r_{ab})} \psi_a \, d\tau$$

$\underbrace{(r_{ab})} \rightarrow$ smatramo
ga fiksiranim

$$\Rightarrow \underline{H_{aa} = E_{1s} - e^2 \left\langle \psi_a \left| \frac{1}{r_b} \right| \psi_a \right\rangle + \frac{e^2}{R}} \qquad (r_{ab} \equiv R)$$

$$[E_{1s} = E_H = -13,6 \, eV = -0,5 \, a.u.]$$

Rezonantni integral:

$$H_{ab} = \langle \psi_a | H | \psi_b \rangle = \left\langle \psi_a \left| -\frac{\hbar^2}{2m}\Delta - \frac{e^2}{r_a} - \frac{e^2}{r_b} + \frac{e^2}{r_{ab}} \right| \psi_b \right\rangle$$

$$= E_{1s} \underbrace{\langle \psi_a | \psi_b \rangle}_{S} - e^2 \left\langle \psi_a \left| \frac{1}{r_a} \right| \psi_b \right\rangle + \frac{e^2}{r_{ab}} \underbrace{\langle \psi_a | \psi_b \rangle}_{S}$$

$$H_{ab} = \left(E_{1s} + \frac{e^2}{R} \right) S - e^2 \left\langle \psi_a \left| \frac{1}{r_a} \right| \psi_b \right\rangle$$

Za nalaženje preostalih integrala S, $I_{aa} = \left\langle \psi_a \left| \frac{e^2}{r_b} \right| \psi_a \right\rangle = I_{bb} = \left\langle \psi_b \left| \frac{e^2}{r_a} \right| \psi_b \right\rangle$

i $I_{ab} = -\left\langle \psi_a \left| \frac{e^2}{r_a} \right| \psi_b \right\rangle$ koriste se eliptičke koordinate.

$$\xi = \frac{r_a + r_b}{R} \quad ; \quad \eta = \frac{r_a - r_b}{R} \quad , \quad \varphi$$

$$\xi \in [1, \infty] \quad ; \quad \eta \in [-1, +1] \quad ; \quad \varphi \in [0, 2\pi]$$

Inverzne su: $r_a = \frac{R}{2}(\xi + \eta) \; ; \; r_b = \frac{R}{2}(\xi - \eta)$

$$d\tau = \frac{R^3}{8}(\xi^2 - \eta^2) \, d\xi \, d\eta \, d\varphi \; ;$$

$$\psi_a \psi_b = \frac{1}{\sqrt{\pi a^3}} e^{-(r_a + r_b)/a} = \frac{1}{\sqrt{\pi a^3}} e^{-R\xi/a}$$

$-e|\psi_a|^2 \rightarrow$ the charge density of the electron

$-e \psi_a \psi_b \rightarrow$ exchange density; this means that electron in some sense is partly in state a and partly in state b, or, in other words, an exchange between these two states takes place. Integrali koji sadrže $\psi_a \psi_b$ nazivaju se izmenski i oni reprezentuju poseban kvantnomeh. efekat.

Rešavanje dvocentričnih integrala

$$J = \int \frac{\exp(-p r_a) \exp(-q r_b)}{r_a r_b} d^3\vec{r}$$

u eliptičnim koordinatama J postaje

$$J = \frac{R}{2} \int_1^\infty d\xi \int_{-1}^{+1} dy \int_0^{2\pi} d\phi \, \exp(-a\xi - by)$$

gde je $a = \frac{R}{2}(p+q)$; $b = \frac{R}{2}(p-q)$

$$\Rightarrow \quad J = \frac{\pi R}{ab} e^{-a}(e^b - e^{-b}) = \frac{4\pi}{R} \frac{1}{p^2 - q^2}(e^{-qR} - e^{-pR})$$

Drugi relevantni integrali dobijaju se diferenciranjem:

$$K = \int \frac{\exp(-p r_a) \exp(-q r_b)}{r_a} d^3\vec{r} = -\frac{\partial}{\partial q} J$$

$$K = \frac{4\pi}{R}\left[\frac{R}{p^2-q^2} e^{-qR} + \frac{2q}{(p^2-q^2)^2}(e^{-pR} - e^{-qR})\right]$$

$$L = \int \exp(-p r_a) \exp(-q r_b) d^3\vec{r} = -\frac{\partial}{\partial p} K$$

$$L = \frac{8\pi}{R(p^2-q^2)^2}\left[R(p e^{-qR} + q e^{-pR}) + \frac{4pq}{p^2-q^2}(e^{-pR} - e^{-qR})\right]$$

Kada je $p = q$

$$J = \frac{4\pi}{R} \lim_{q\to p} \frac{e^{-qR} - e^{-pR}}{p^2 - q^2} = \frac{4\pi}{R} R \frac{e^{-pR}}{2p} = \frac{2\pi}{p} e^{-pR}$$

$$K = \frac{4\pi}{R} \lim_{q\to p} \frac{R(p^2-q^2)e^{-qR} + 2q(e^{-pR} - e^{-qR})}{(p^2-q^2)^2}$$

$$K = \frac{4\pi}{R} \lim_{q\to p} \frac{R 2p e^{-qR} - R 2q e^{-pR}}{2(p^2-q^2)2p} = 2\pi \lim_{q\to p} \frac{p e^{-qR} - q e^{-pR}}{p(p^2-q^2)}$$

$$K = 2\pi \lim_{q\to p} \frac{e^{-qR} + Rq e^{-pR}}{p^2 - q^2 + p \cdot 2p} = \frac{\pi}{p^2}(1 + pR)e^{-pR}$$

Slično:

$$L = \frac{\pi}{p^3}\left(1 + pR + \frac{1}{3}p^2R^2\right)e^{-pR}$$
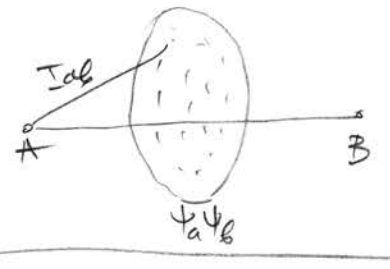
Koristedi rešenja integrala na str. 15 imamo:

$$S = \langle \psi_a | \psi_B \rangle = \left\{ 1 + \frac{ZR}{a} + \frac{1}{3}\left(\frac{ZR}{a}\right)^2 \right\} e^{-ZR/a} \quad (Z=1)$$

$$I_{ab} = \frac{e^2}{a}\left\{ 1 + \frac{R}{a} \right\} e^{-R/a} \quad \Longleftarrow \quad = e^2 \int \psi_a \frac{1}{r_a} \psi_b \, d\tau \quad (\equiv k')$$

I_{ab} - predstavlja energiju razmene ili energiju rezonancije. Možei ovamo to je interaction of the overlap charge density $-e\psi_a \psi_b$ sa nukleusom A

$$I_{aa} = e^2 \int \psi_a \left(\frac{1}{r_b}\right) \psi_a \, d\tau = I_{bb} = -e^2 \int \psi_b \left(\frac{1}{r_a}\right) \psi_b \, d\tau$$

$$= \frac{e^2}{R}\left[1 - e^{-2R/a}\left(1 + \frac{R}{a} \right) \right] \quad (\equiv j')$$
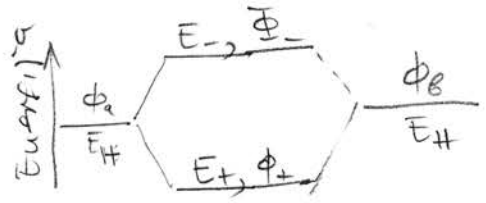
Sada možemo da pišemo simetrični i antisimetrični izraz za energiju

$$E_S \equiv E_+ = \frac{H_{aa} + H_{ab}}{1+S} = E_H + \frac{e^2}{R} - \frac{I_{aa} + I_{ab}}{1+S}$$

$$E_A \equiv E_- = \frac{H_{aa} - H_{ab}}{1+S} = E_H + \frac{e^2}{R} - \frac{I_{aa} - I_{ab}}{1-S}$$

Oba integrala I_{aa} i I_{ab} su pozitivna, sa $I_{aa} > I_{ab}$.
Niža energija je E_S (E_+) i ta orbitela je $\Phi_S (\equiv \Phi_+)$
i naziva se vezivna orbitela, gornja je antibonding orbitel.

Simetrično stanje odgovara stabilnosti molekula

Ne zaboravimo: vezivanje u molekule nastaje kod elektroni dolaze u energetska stanja koja su niža nego kod slobodnih atoma.

Energija disocijacije je razlika između minimalne energije u ravnotežnom stanju i energije na distanci $R(=r_{ab}) \to \infty$
ovakva teorija daje minimum na $R \approx 1,32 \text{Å}$ i $1,76 \, eV$
a eksp. vrednosti su $1,06 \text{Å}$ i $2,79 \, eV$.
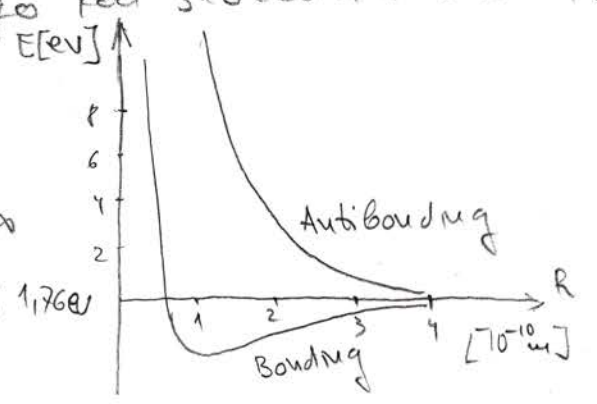
Laplasijan u eliptičkim koordinatama (confocal eliptic coordinates):

$$\Delta = \nabla^2 = \frac{4}{R^2(\xi^2-\eta^2)}\left\{\frac{\partial}{\partial\xi}\left[(\xi^2-1)\frac{\partial}{\partial\xi}\right] + \frac{\partial}{\partial\eta}\left[(1-\eta^2)\frac{\partial}{\partial\eta}\right] + \frac{\xi^2-\eta^2}{(\xi^2-1)(1-\eta^2)}\frac{\partial^2}{\partial\varphi^2}\right\}$$

Šr. j-na $\left(-\frac{1}{2}\Delta - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R} - E\right)\Phi = 0$

$$\frac{\partial}{\partial\xi}\left[(\xi^2-1)\frac{\partial\Phi}{\partial\xi}\right] + \frac{\partial}{\partial\eta}\left[(1-\eta^2)\frac{\partial\Phi}{\partial\eta}\right] + \left(\frac{1}{\xi^2-1} + \frac{1}{1-\eta^2}\right)\frac{\partial^2\Phi}{\partial\varphi^2} + 2R^2\left[\frac{1}{4}\left(E-\frac{1}{R}\right)(\xi^2-\eta^2) + \frac{1}{R}\xi\right]\Phi =$$

Rešenje tražimo u vidu proizvoda:

$$\Phi(\xi,\eta,\varphi) = F(\xi)G(\eta)e^{im\varphi}, \quad m = 0, \pm 1, \pm 2, \dots$$

gde su f-je $F(\xi)$ i $G(\eta)$ su normalizabilna rešenja
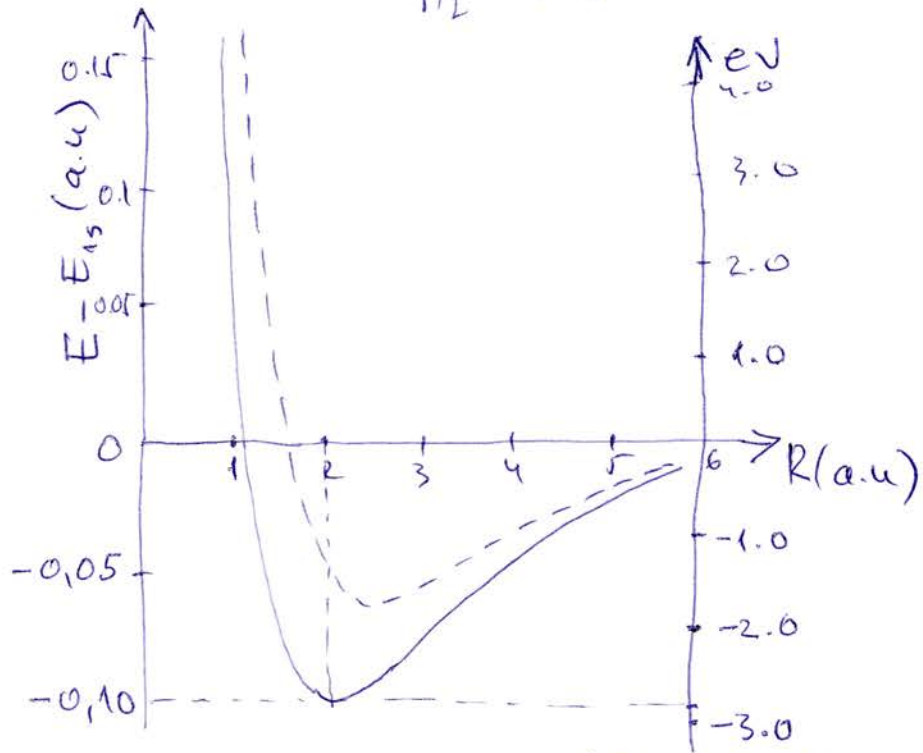
j-na: $\frac{d}{d\xi}\left[(\xi^2-1)\frac{dF}{d\xi}\right] + \left[\frac{R^2}{2}\left(E-\frac{1}{R}\right)\xi^2 + 2R\xi - \frac{m^2}{\xi^2-1} + \mu\right]F(\xi) = 0 \quad \cdots (1)$

$\frac{d}{d\eta}\left[(1-\eta^2)\frac{dG}{d\eta}\right] - \left[\frac{R^2}{2}\left(E-\frac{1}{R}\right)\eta^2 + \frac{m^2}{1-\eta^2} + \mu\right]G(\eta) = 0 \quad \cdots (2)$

μ - separaciona konstanta. Svaki elektronski term je okarakterisan sa tri kv. broja $\lambda = |m|$, n_ξ, n_η što predstavljaju nule f-ja $F(\xi)$ i $G(\eta)$.
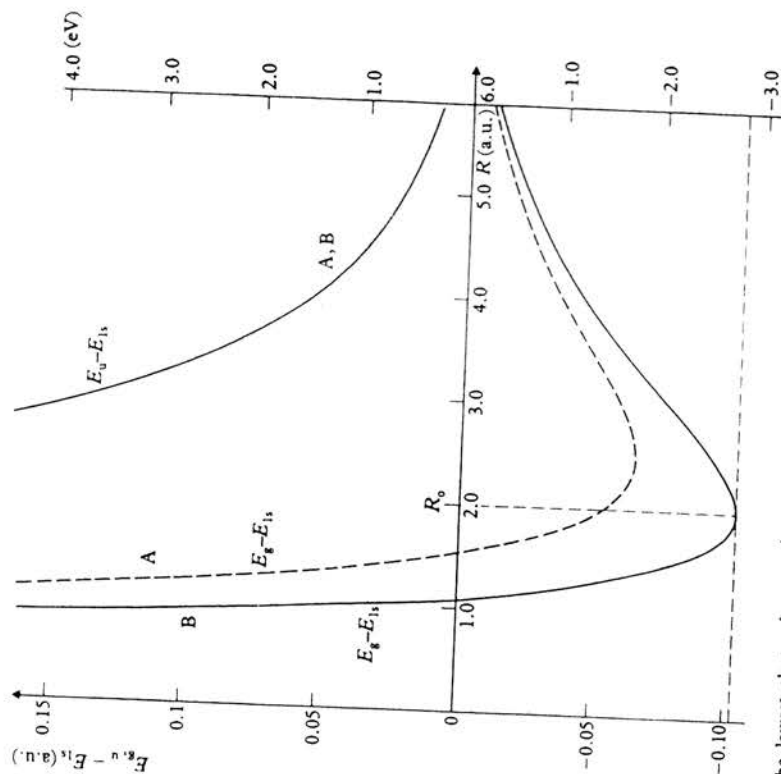
J-ne (1) i (2) mogu da se reše numerički za osnovno i pobuđena stanja. To su prvo uradili 1953. D. Bates, K. Ledsham i A. Stewart

H_2^+ $(\sigma_g 1s)$ lowest σ_g state)

----- LCAO $\rightarrow$ $\begin{cases} \text{(Energija disociacije} \\ De = E_{1s} - E_g(R_0) = 0,065 \text{ a.u} = 1,77 \text{ ov}) \\ (R_0 = 2,49 \text{ a.u} = 1,32\text{Å}) \end{cases}$

——— exact values $\qquad (E \equiv E_g)$

$\qquad\qquad \llcorner\!\rightarrow \begin{cases} De = E_{1s} - E_g(R_0) = 0,103 \text{ a.u} = 2,79 \text{ eV} \\ R_0 = 1,06 \text{ Å} \end{cases}$

$1 a_0 = 0,529 \text{ Å}$

Molecular structure

9.9 The lowest electronic potential energy curves of H_2^+. The dashed lines labelled A, show $(E_g(R) - E_{1s})$ and $(E_u(R) - E_{1s})$ calculated using the simple LCAO wave functions of [9.47], while the solid curves labelled B show the exact values of the same quantities calculated from equations [9.61] to [9.64].

an attraction leading to the formation of a stable molecular ion. The corresponding molecular orbital Φ_g given by [9.47a] is said to be a *bonding molecular orbital*. In the present case it is an approximation to the ground state (that is, the lowest σ_g state) and is designated $\sigma_g 1s$.

In contrast, we see from Fig. 9.9 that the function $E_u(R)$ has no minimum and is repulsive at all distances; a molecule in this state will immediately dissociate into a proton and a hydrogen atom in the 1s state. The corresponding molecular orbital Φ_u (see (9.47b)) is called an *antibonding* orbital, and is denoted in the present case by $\sigma_u^\star 1s$, where the superscript (*) indicates that we are dealing with an antibonding orbital.

It is worth noting that the term H_{AB}, in which the matrix element of the Hamiltonian H between atomic orbitals centred on the protons A and B is evaluated, plays a vital role in obtaining bonding for the $\sigma_g 1s$ state. If this term

Electronic structure of diatomic molecules

were ignored, the two functions $E_g(R)$ and $E_u(R)$ would coincide, the resulting curve being repulsive at all distances.

The electron probability density in the states Φ_g and Φ_u is given by $|\Phi_g|^2$ and $|\Phi_u|^2$, respectively, so that the corresponding charge densities are $\rho_g = -e|\Phi_g|^2$ and $\rho_u = -e|\Phi_u|^2$ (or $\rho_g = -|\Phi_g|^2$ and $\rho_u = -|\Phi_u|^2$ in atomic units). If the charge density ρ_g is evaluated at points between A and B along the internuclear line, it is found to be greater (in absolute value) than the sum of the densities due to two isolated H atoms with their protons placed at A and B, normalised so that half an electron is associated with each proton. It is this *excess of negative charge* between the protons which causes the binding (or bonding). On the other hand, if the charge density ρ_u corresponding to the antibonding case is evaluated, a *deficiency of negative charge* is found between the protons. This is clearly seen in Fig. 9.10 where the wave functions Φ_g and Φ_u as well as the absolute value of the charge densities ρ_g and ρ_u are plotted along the internuclear line.

The *exact* binding energy of H_2^+ is a little greater than the result obtained above, with $D_e = E_{1s} - E_g(R_0) = 0.103$ a.u. $= 2.79$ eV, and the true equilibrium distance is $R_0 = 1.06$ Å. The principal failing of the approximate wave function $\Phi_g(\mathbf{R}; \mathbf{r})$ given by [9.47a] is that at small separations Φ_g should approach the wave function of $He^+(1s)$, the ground state of the positive helium ion with nuclear charge $Z = 2$, and in the approximation [9.47a] it does not. This defect can be remedied by using orbitals of variable charge, such as

$$u_{1s}(Z^\star, r) = \left(\frac{Z^{\star 3}}{\pi}\right)^{1/2} e^{-Z^\star r} \qquad [9.58]$$
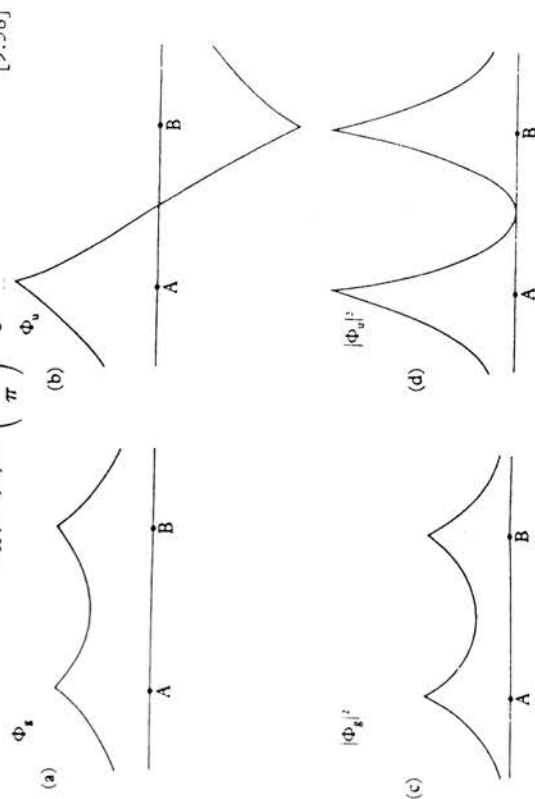
9.10 Wave functions Φ_g and Φ_u and charge densities $|\Phi_g|^2$, $|\Phi_u|^2$ for the hydrogen molecular ion H_2^+, plotted along the internuclear line to an arbitrary scale. The points A and B represent the positions of the two protons.