Teori Kuantum untuk Material
Bagian #02-1

- Pemecahan Persamaan Schrödinger
  - Atom Hidrogen
  - Atom Berelektron Banyak

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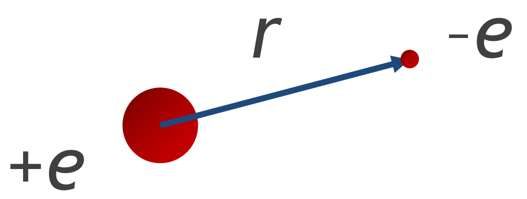
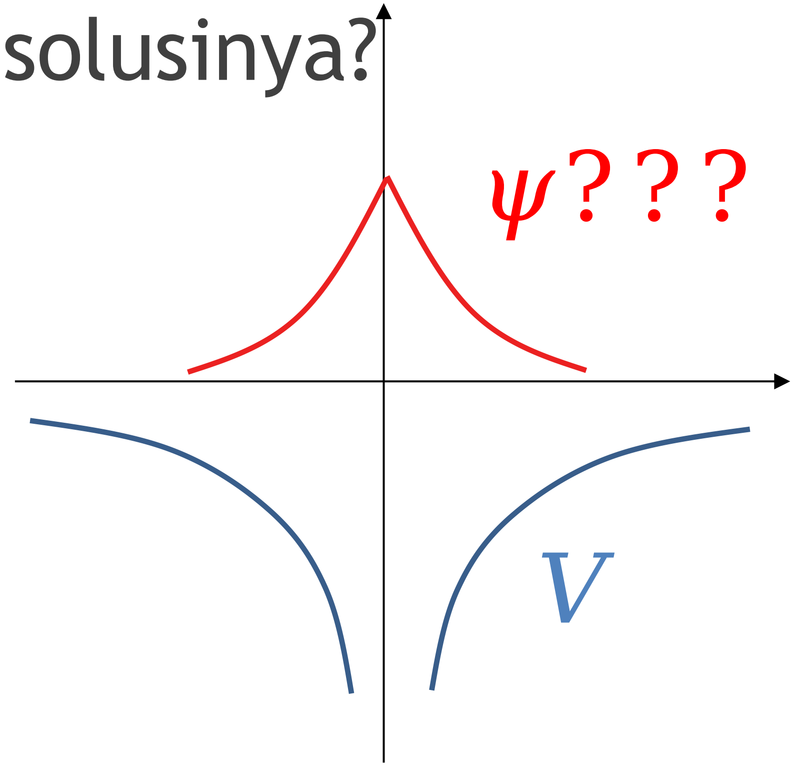
Atom hidrogen

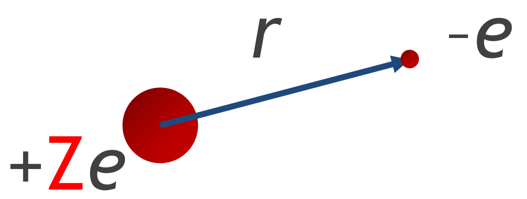


Persamaan Schrödinger: $\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)-\frac{e^2}{|\vec{r}|}\right]\psi(\vec{r}) = E\psi(\vec{r})$

Bagaimana kira-kira solusinya?

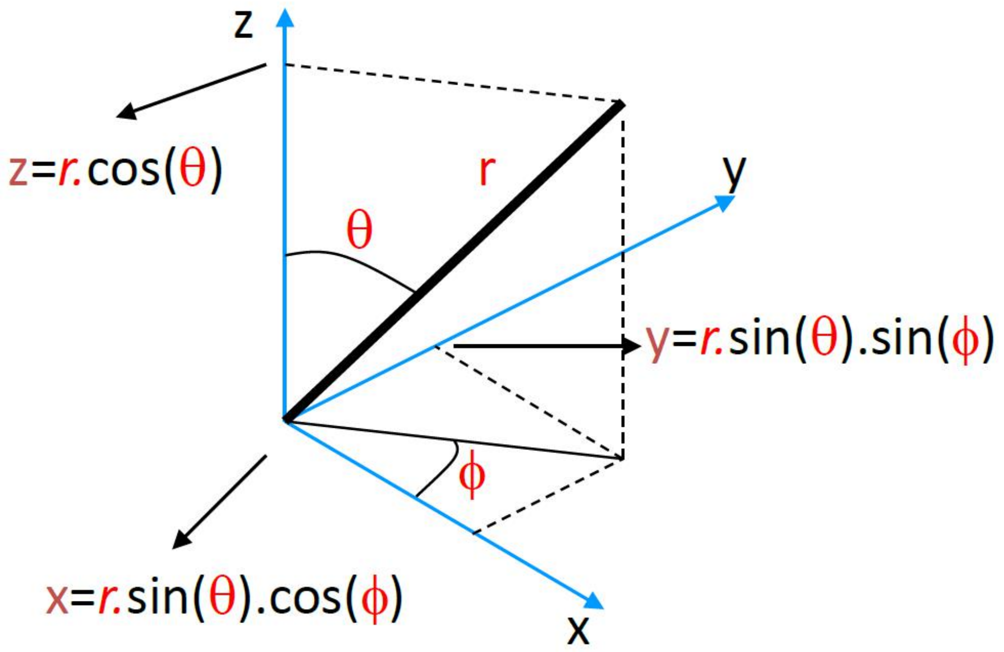


Lebih rumit sedikit...



Atom mirip hidrogen: $\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)-\frac{Ze^2}{|\vec{r}|}\right]\psi(\vec{r}) = E\psi(\vec{r})$

Potensial hanya bergantung $|\vec{r}|$ $(= r)$



Koordinat bola lebih memudahkan

Suatu titik pada ruang 3D dapat direpresentasikan oleh:

- Tiga koordinat Kartesian x, y, z **atau**
- Sudut θ & φ dan radius r

Atom mirip hidrogen

Kita perlu pecahkan persamaan Schrödinger dalam koordinat bola

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}+\frac{\cos\theta}{r^2\sin\theta}\frac{\partial}{\partial\theta}+\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}\right)-\frac{Ze^2}{r}\right]\psi(\mathrm{r},\phi,\theta)=E\psi(r,\phi,\theta)$$

Coba solusi dengan pemisahan variabel:

$$\psi(r,\phi,\theta)=R(r)\Phi(\phi)\Theta(\theta)$$

Fokus dulu pada solusi fungsi gelombang keadaan dasar

Bagian sudut: $\Phi(\phi)=\Theta(\theta)=1$

Atom mirip hidrogen

Masukkan $\Phi(\phi) = \Theta(\theta) = 1$ ke persamaan atom hidrogen:

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}+\frac{\cos\theta}{r^2\sin\theta}\frac{\partial}{\partial\theta}+\frac{1}{r^2}\frac{\partial^2}{\partial\theta^2}\right)-\frac{Ze^2}{r}\right]\psi(\mathrm{r},\phi,\theta) = E\psi(r,\phi,\theta)$$

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)-\frac{Ze^2}{r}\right]R(r) = ER(r)$$

Fungsi percobaan: $R(r) = A\exp\left(-\frac{r}{a}\right)$ $\Rightarrow$ $\frac{\partial R}{\partial r} = -\frac{A}{a}\exp\left(-\frac{r}{a}\right)$

$$\Rightarrow \frac{\partial^2 R}{\partial r^2} = +\frac{A}{a^2}\exp\left(-\frac{r}{a}\right)$$

Silakan bisa buktikan: $-\frac{\hbar^2}{2m}\left(\frac{1}{a^2}-\frac{2}{ra}\right)-\frac{Ze^2}{r} = E$?

Atom mirip hidrogen

Kelompokkan variabel dan konstanta: $\frac{1}{r}\left(\frac{\hbar^2}{ma} - Ze^2\right) = E + \frac{\hbar^2}{2ma^2}$

Solusi diperoleh hanya ketika kedua ruas bernilai nol

$$\boxed{\frac{\hbar^2}{ma} - Ze^2 = 0}$$

$$\Rightarrow \quad a = \frac{1}{Z}\frac{\hbar^2}{e^2 m} = \frac{a_0}{Z}$$

Radius Bohr a_0 (ukuran atom):

$$\sim 0.53 Å$$

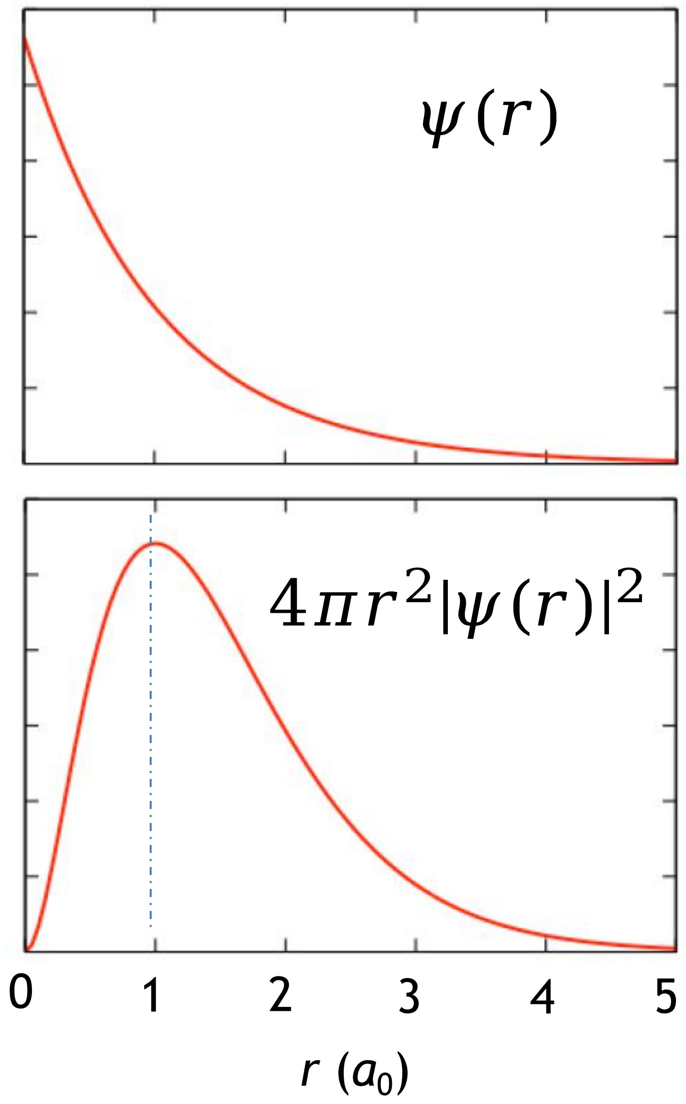
$$\boxed{0 = E + \frac{\hbar^2}{2ma^2}}$$

$$\Rightarrow \quad E = -\frac{1}{2m}\left(\frac{\hbar}{a}\right)^2 = -\frac{1}{2m}\left(\frac{Z\hbar}{a_0}\right)^2$$

$$= -\frac{1}{2ma}\left(\frac{\hbar^2}{a}\right) = -\frac{1}{2}\frac{Ze^2}{a}$$

$$= -\frac{1}{2}\frac{Z^2e^2}{a_0}$$

Keadaan dasar atom hidrogen



Fungsi gelombang keadaan dasar:

$$\psi(r) = A\exp\left(-\frac{r}{a_0}\right)$$

Radius Bohr:

$$a_0 = \frac{\hbar^2}{e^2 m} = 0.529177040.53\text{Å}$$

Energi total: $\langle K \rangle + \langle V \rangle$

$$E = -\frac{1}{2}\frac{e^2}{a_0} = -13.6058\ \text{eV}$$

Energi Hartree: $-\langle V \rangle$

$$1\text{Ha} = 2\text{Ry} = \frac{e^2}{a_0} = 27.21161\ \text{eV}$$

Keadaan tereksitasi pada atom hidrogen

Separasi variabel dan asumsikan tidak ada kebergantungan sudut

$$\psi(r, \phi, \theta) = R(r)\Phi(\phi)\Theta(\theta)$$

$$\Phi(\phi) = \Theta(\theta) = 1$$

Persamaan diferensial untuk bagian radial:

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) - \frac{Ze^2}{r}\right] R(r) = E R(r)$$

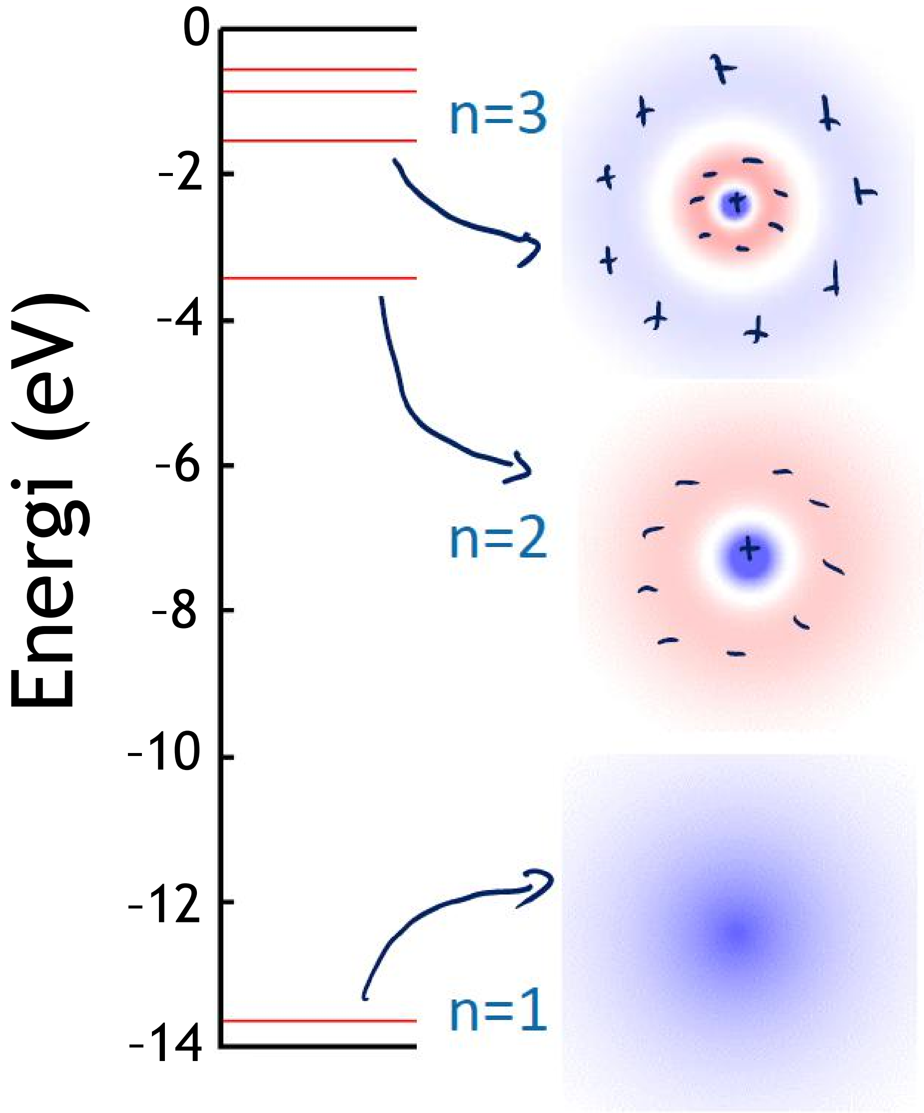
Permasalahan nilai eigen memberikan *n* solusi radial

$$R_n(r)$$

$$E_n = -\frac{13.6\ \text{eV}}{n^2} Z^2$$

n adalah bilangan kuantum utama

Solusi radial beberapa tingkat hidrogen



Keadaan-keadaan ini disebut “s”

2 simpul $E \sim\ -1.51\ \mathrm{eV}$

1 simpul $E \sim\ -3.4\ \ \mathrm{eV}$

0 simpul $E \sim\ -13.6\ \ \mathrm{eV}$

Kuis #4

- Bagaimana hubungan antara jumlah simpul dari fungsi gelombang hidrogen dengan bilangan kuantum utama *n*?

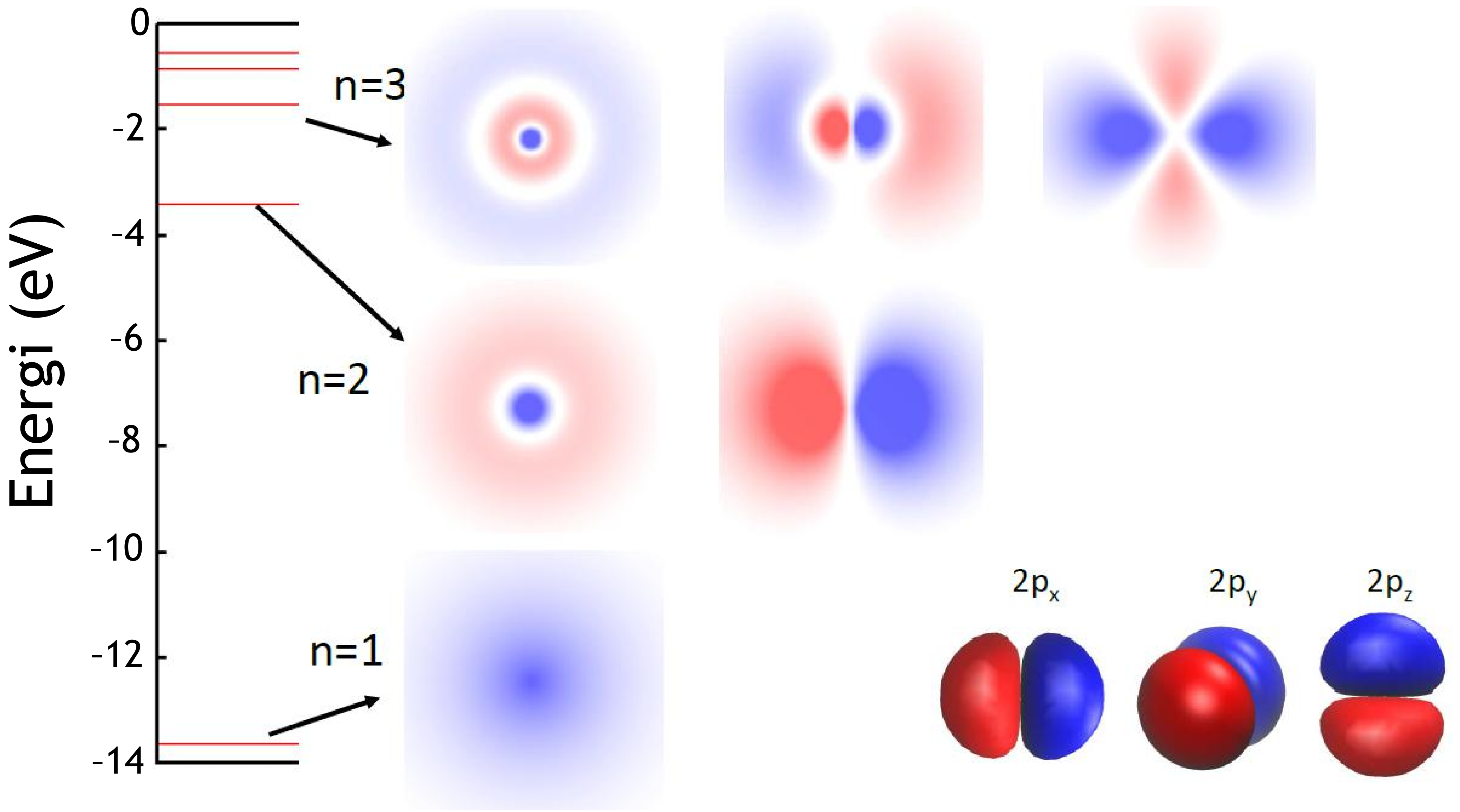
(A) Jumlah simpul tidak terkait dengan bilangan kuantum utama.

(B) Jumlah simpul diberikan oleh *n*.

(C) Jumlah simpul diberikan oleh n – 1.

(D) Baik-baik saja.

Bentuk lengkap fungsi gelombang hidrogen



Solusi umum

$$\psi_{n,l,m}(r,\theta,\phi) = R_{nl}(r)Y_{l,m}(\phi,\theta)$$

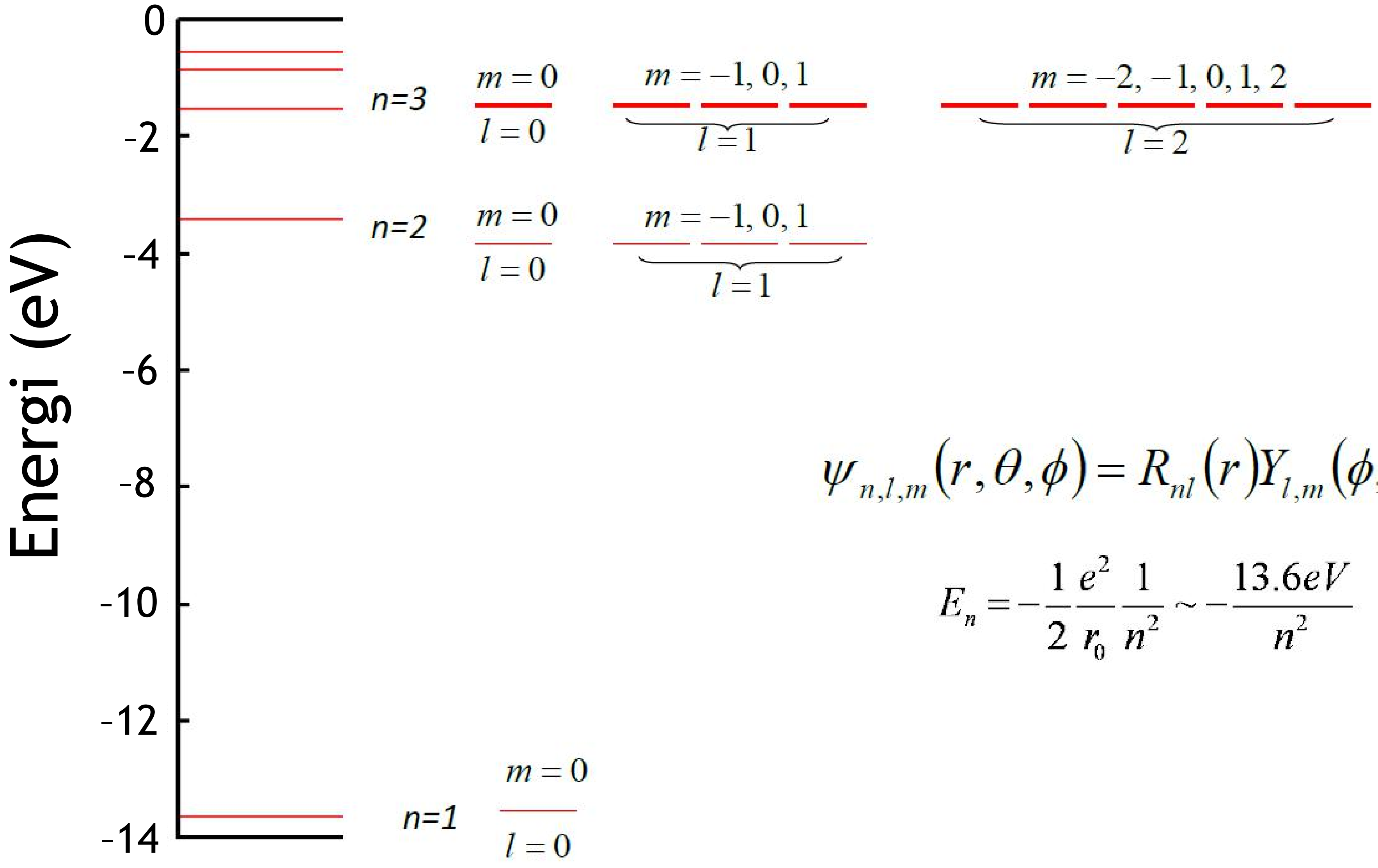
Bilangan kuantum yang muncul:

- n : bilangan kuantum utama
  - Energi bergantung pada n

$$E_n = -\frac{13.6}{n^2}Z^2$$

- l : bilangan kuantum momentum sudut
  - Nilainya dibatasi bilangan kuantum utama: $0,\ 1,\ \ldots,\ n-1$
- m: bilangan kuantum magnetic (proyeksi l pada sumbu z)
  - Nilainya dibatasi l yakni $m = -l, -l+1,\ \ldots,\ l-1, l$

Solusi umum



$$\psi_{n,l,m}(r,\theta,\phi)=R_{nl}(r)Y_{l,m}(\phi,\theta)$$

$$E_n=-\frac{1}{2}\frac{e^2}{r_0}\frac{1}{n^2}\sim-\frac{13.6eV}{n^2}$$

Tabel fungsi gelombang atom hidrogen

Table 3.1. *States of one-electron atoms*

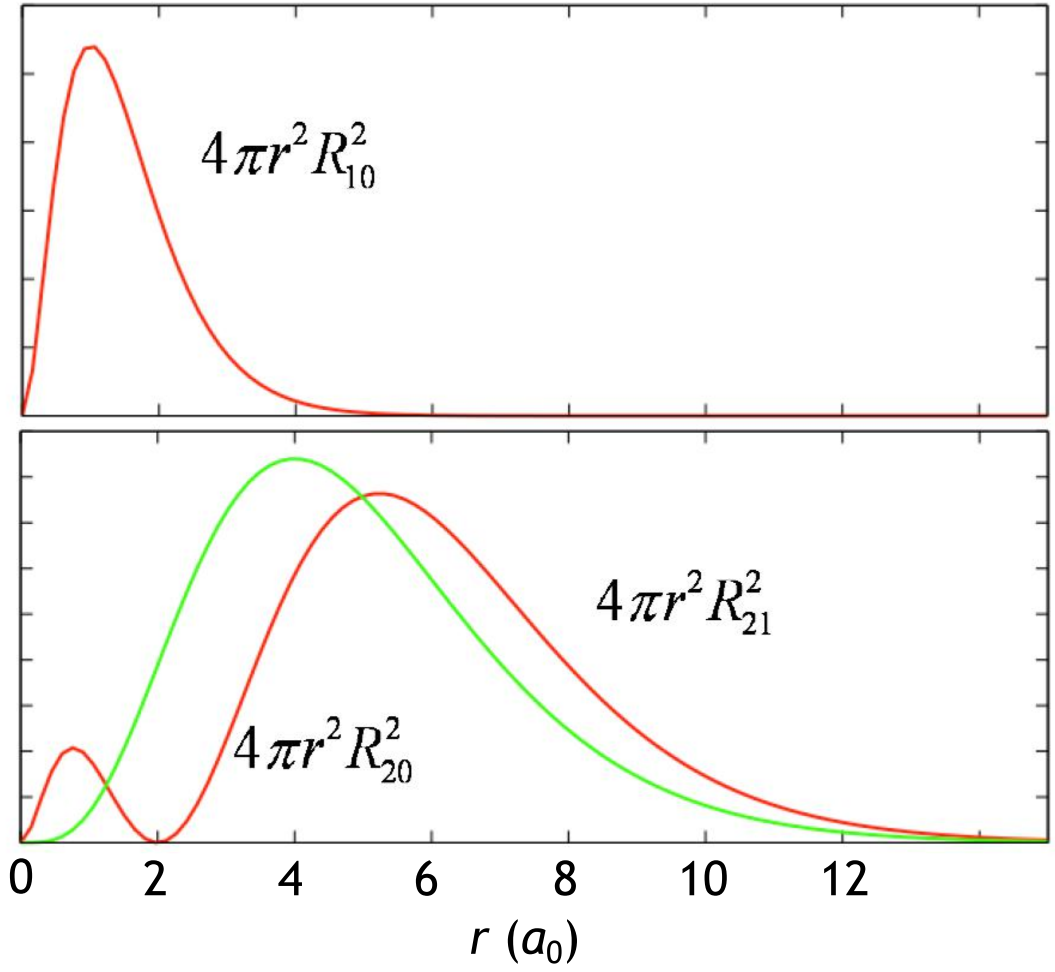
n	l	$\lvert m \rvert$	Spectroscopic designation	E_n in units of $e^2/2a_0$	g	$\psi_{n,l,m}(r, \theta, \phi)$
1	0	0	$1s$	-1	1	$N_1 \exp(-Zr/a_0)$
2	0	0	$2s$	$-\frac{1}{4}$		$N_2(2 - Zr/a_0) \exp(-Zr/2a_0)$
2	1	0	$2p_z$	$-\frac{1}{4}$	4	$N_2(Zr/a_0) \exp(-Zr/2a_0) \cos\theta$
2	1	1, cos	$2p_x$	$-\frac{1}{4}$		$N_2(Zr/a_0) \exp(-Zr/2a_0) \sin\theta \cos\phi$
2	1	1, sin	$2p_y$	$-\frac{1}{4}$		$N_2(Zr/a_0) \exp(-Zr/2a_0) \sin\theta \sin\phi$
3	0	0	$3s$	$-\frac{1}{9}$		$N_3[27 - 18(Zr/a_0) + 2(Zr/a_0)^2] \exp(-Zr/3a_0)$
3	1	0	$3p_z$	$-\frac{1}{9}$		$N_3\sqrt{6}\,(6 - Zr/a_0)(Zr/a_0) \exp(-Zr/3a_0) \cos\theta$
3	1	1, cos	$3p_x$	$-\frac{1}{9}$		$N_3\sqrt{6}\,(6 - Zr/a_0)(Zr/a_0) \exp(-Zr/3a_0) \sin\theta \cos\phi$
3	1	1, sin	$3p_y$	$-\frac{1}{9}$	9	$N_3\sqrt{6}\,(6 - Zr/a_0)(Zr/a_0) \exp(-Zr/3a_0) \sin\theta \sin\phi$
3	2	0	$3d_{3z^2-r^2}$	$-\frac{1}{9}$		$N_3\sqrt{1/2}(Zr/a_0)^2 \exp(-Zr/3a_0)(3\cos^2\theta - 1)$
3	2	1, cos	$3d_{xz}$	$-\frac{1}{9}$		$N_3\sqrt{6}(Zr/a_0)^2 \exp(-Zr/3a_0) \sin\theta \cos\theta \cos\phi$
3	2	1, sin	$3d_{yz}$	$-\frac{1}{9}$		$N_3\sqrt{6}(Zr/a_0)^2 \exp(-Zr/3a_0) \sin\theta \cos\theta \sin\phi$
3	2	2, cos	$3d_{x^2-y^2}$	$-\frac{1}{9}$		$N_3\sqrt{3/2}(Zr/a_0)^2 \exp(-Zr/3a_0) \sin^2\theta \cos 2\phi$
3	2	2, sin	$3d_{xy}$	$-\frac{1}{9}$		$N_3\sqrt{3/2}(Zr/a_0)^2 \exp(-Zr/3a_0) \sin^2\theta \sin 2\phi$

$$N_1 = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2}, \quad N_2 = \frac{1}{4}\left(\frac{Z^3}{2\pi a_0^3}\right)^{1/2}, \quad N_3 = \frac{1}{81}\left(\frac{Z^3}{3\pi a_0^3}\right)^{1/2}$$

Martin Karplus and Richard N. Porter
Atoms and molecules: an introduction for students of physical chemistry

Atom berelektron banyak

- Orbital-orbital menjaga bentuk yang sama seperti hidrogen



- Efek perisai:

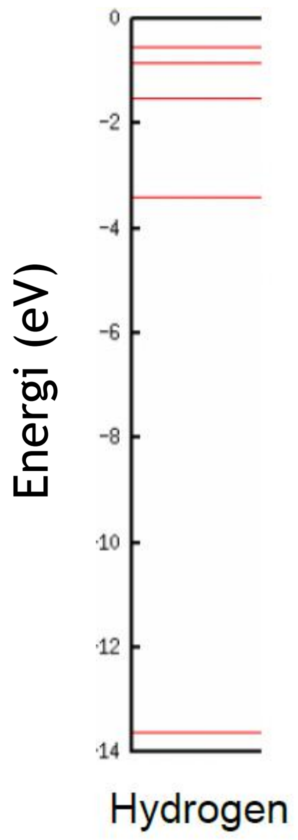
  Elektron di kulit dalam melindungi potensial inti dari elektron luar

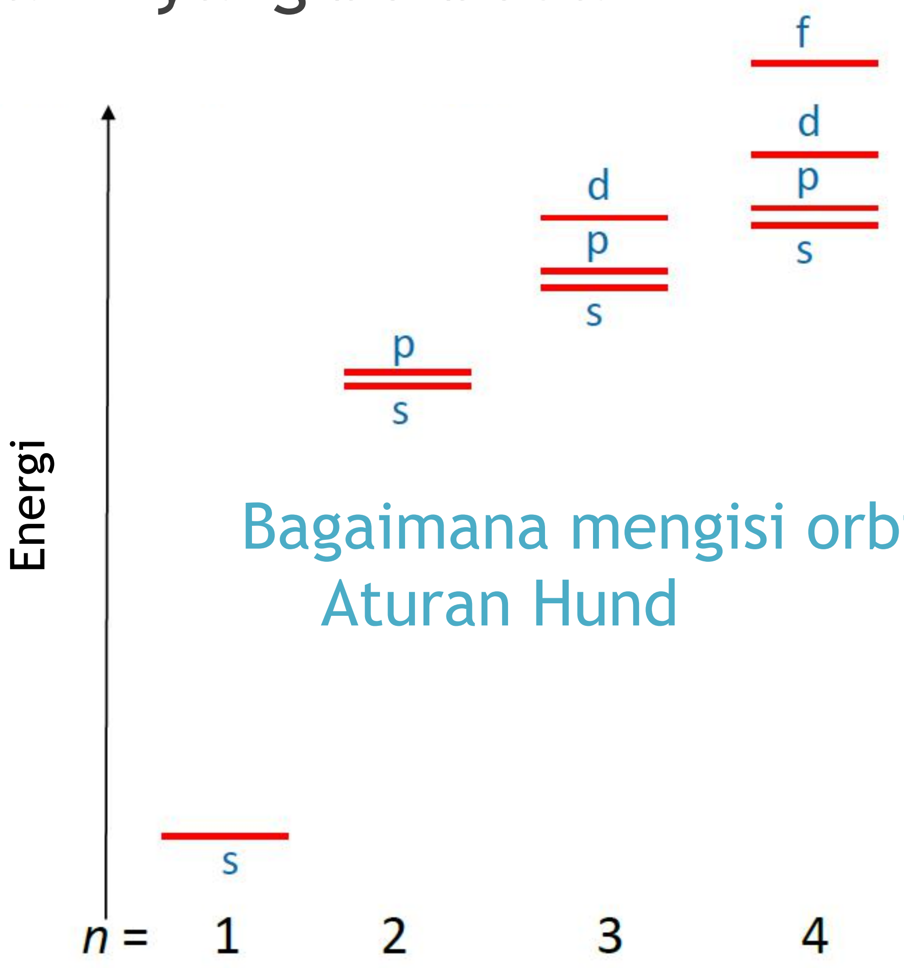
  Energi tidak hanya bergantung pada n, tetapi juga pada l

  Semakin besar bilangan momentum sudut, semakin besar energinya

Tingkat-tingkat energi

- Efek perisai menyebabkan perbedaan energi orbital yang memiliki n yang sama dan l yang berbeda





Bagaimana mengisi orbital ini?
Aturan Hund

Kuis #5

	1s	2s	2p		
H					
He					
Li	↑↓				
Be	↑↓				
B	↑↓	↑↓			
C	↑↓	↑↓			
N	↑↓	↑↓			
O	↑↓	↑↓			
F	↑↓	↑↓			
Ne	↑↓	↑↓			

Lengkapi diagram di samping sesuai aturan Hund!

Komputasi mekanika kuantum hidrogen

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\right]\Psi(r) = E\Psi(r)$$

Use atomic units:

Mass:	m_e
Charge:	e
Distance:	$a_0 = \frac{\hbar^2}{e^2 m_e} \sim 0.52918\ \text{Å}$
Energy:	$h_0 = \frac{e^2}{a_0} \sim 27.21161\ eV$

Schrödinger equation in atomic units:

$$\left[-\frac{1}{2}\nabla^2 - \frac{1}{r}\right]\Psi(r) = E\Psi(r)$$

Komputasi mekanika kuantum hidrogen

Expand the WF as a linear combination of known functions (basis set)

Unknown coefficients

$$\Psi(r) = \sum_{i=1}^{N} c_i \chi_i$$

Known functions (basis set)

Plug in this WF into the Schrödinger equation

$$\left[-\frac{1}{2}\nabla^2 - \frac{1}{r}\right]\sum_{i=1}^{N} c_i \chi_i = E \sum_{i=1}^{N} c_i \chi_i$$

Komputasi mekanika kuantum hidrogen

$$\left[-\frac{1}{2}\nabla^2 - \frac{1}{r}\right]\sum_{i=1}^{N} c_i\chi_i = E\sum_{i=1}^{N} c_i\chi_i$$

Multiply by χ_j^* from left and integrate over all space

$$\sum_{i=1}^{N} c_i\chi_j^*\left[-\frac{1}{2}\nabla^2 - \frac{1}{r}\right]\chi_i = E\sum_{i=1}^{N} c_i\chi_j^*\chi_i$$

$$\sum_{i=1}^{N} c_i\underbrace{\int \chi_j^*\left[-\frac{1}{2}\nabla^2 - \frac{1}{r}\right]\chi_i dr^3}_{\text{Hamiltonian term (can be evaluated since the basis functions are known)}} = E\sum_{i=1}^{N} c_i\underbrace{\int \chi_j^*\chi_i dr^3}_{\text{Overlap between orbitals}}$$

Komputasi mekanika kuantum hidrogen

$$\sum_{i=1}^{N} c_i \underbrace{\int \chi_j^* \left[-\frac{1}{2}\nabla^2 - \frac{1}{r}\right] \chi_i dr^3}_{H_{ij}} = E \sum_{i=1}^{N} c_i \underbrace{\int \chi_j^* \chi_i dr^3}_{S_{ij}}$$

$$\sum_{i=1}^{N} H_{ij} c_i = E \sum_{i=1}^{N} S_{ij} c_i$$

Generalized eigenvalue problem

Secular equation: $Hc = ESc$

Komputasi mekanika kuantum hidrogen

How to choose a good basis set?

$$\Psi(r) = \sum_{i=1}^{N} c_i \chi_i$$

Shape: similar to the actual WF

$$H_{ij} = \int \chi_j^* \left[-\frac{1}{2}\nabla^2 - \frac{1}{r} \right] \chi_i dr^3$$

Integrals computable analytically

$$S_{ij} = \int \chi_j^* \chi_i dr^3$$

Komputasi mekanika kuantum hidrogen

Gaussian basis set

$$\chi_i(\vec{r}) = \exp(-\alpha_i r^2) \qquad \Psi(r) = \sum_{i=1}^{N} c_i \exp(-\alpha_i r^2)$$

$$T_{ij} = -\frac{1}{2}\int \chi_j^* \nabla^2 \chi_i dr^3 = 3\frac{\alpha_i \alpha_j \pi^{3/2}}{(\alpha_i + \alpha_j)^{5/2}}$$

Kinetic energy

$$V_{ij} = -\int \chi_j^* \frac{1}{r} \chi_i dr^3 = -\frac{2\pi}{\alpha_i + \alpha_j}$$

Potential energy

$$S_{ij} = \int \chi_j^* \chi_i dr^3 = \left(\frac{\pi}{\alpha_i + \alpha_j}\right)^{3/2}$$

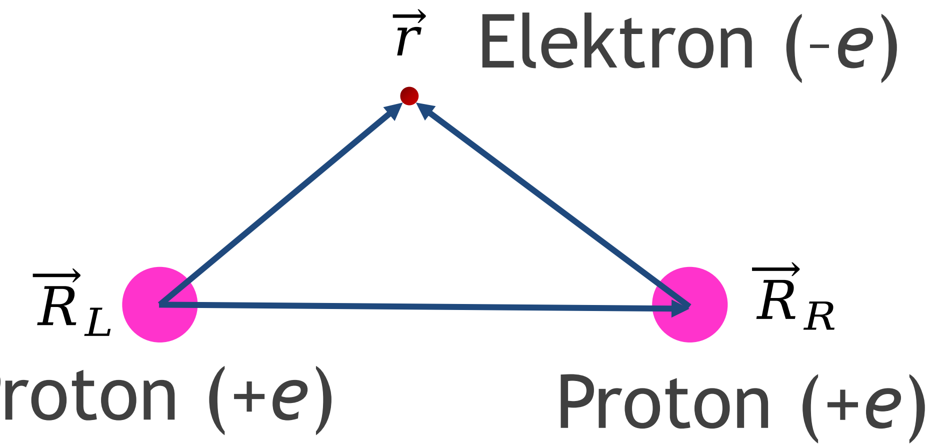
Overlap

Teori Kuantum untuk Material Bagian #02-2

- Ikatan Kimia
- Molekul hidrogen
- Metode LCAO

Molekul Paling Sederhana

H_2^+



Hamiltonian Born-Oppenheimer:

$$H = -\frac{\hbar^2}{2m}\vec{\nabla}_r^2 - \frac{e^2}{\left|\vec{r} - \vec{R}_L\right|} - \frac{e^2}{\left|\vec{r} - \vec{R}_R\right|} + \frac{e^2}{\left|\vec{R}_R - \vec{R}_L\right|}$$

Fungsi gelombang H_2^+

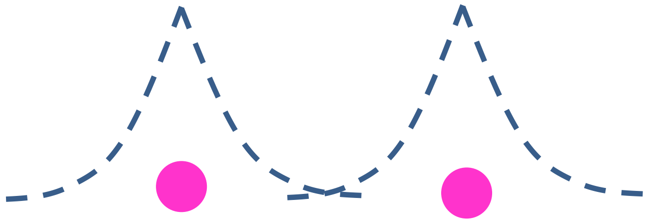
Jika dua proton berjauhan:

atau:

$$\psi_{1s}\left(\vec{r}-\vec{R}_L\right)=\psi_L$$

$$\psi_{1s}\left(\vec{r}-\vec{R}_R\right)=\psi_R$$

Jika dua proton berdekatan:



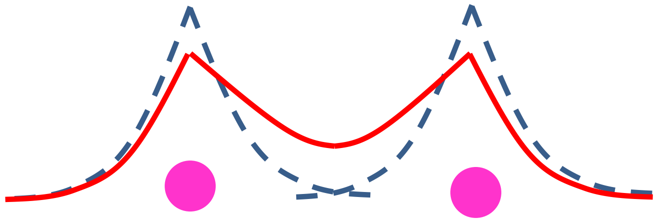
Orbital molekuler

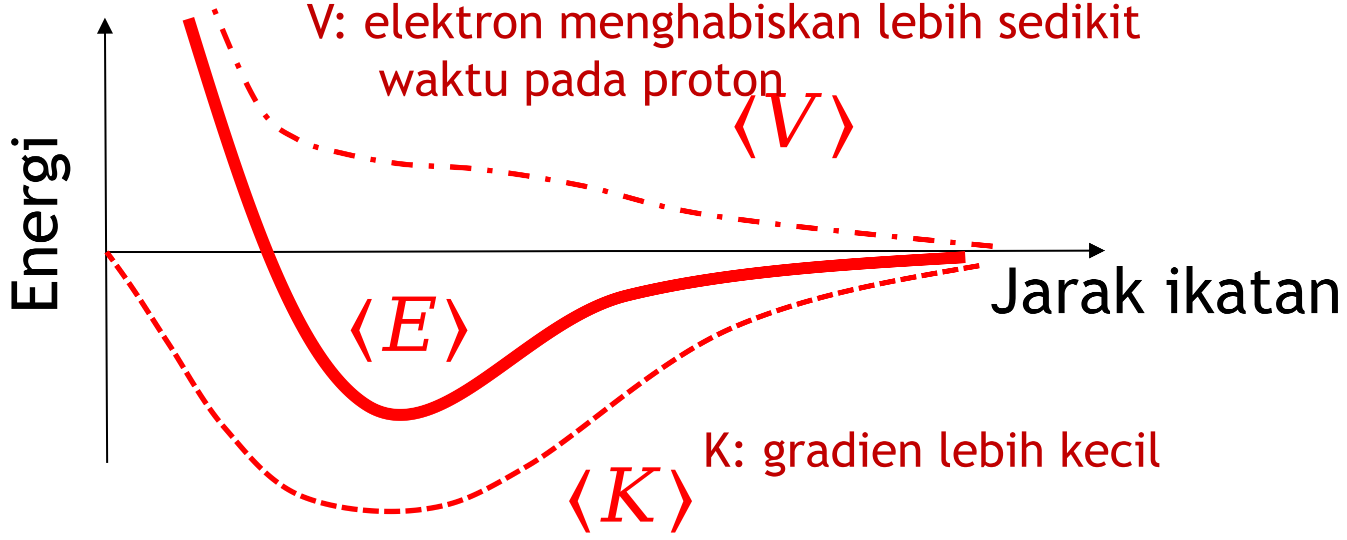
Kombinasi linear orbital atomik (LCAO)

$$\psi_{MO}=a_L\psi_L+a_R\psi_R$$

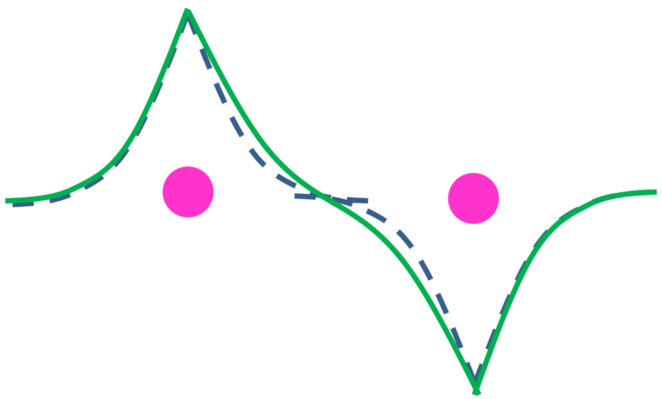
Solusi intuitif untuk H_2^+

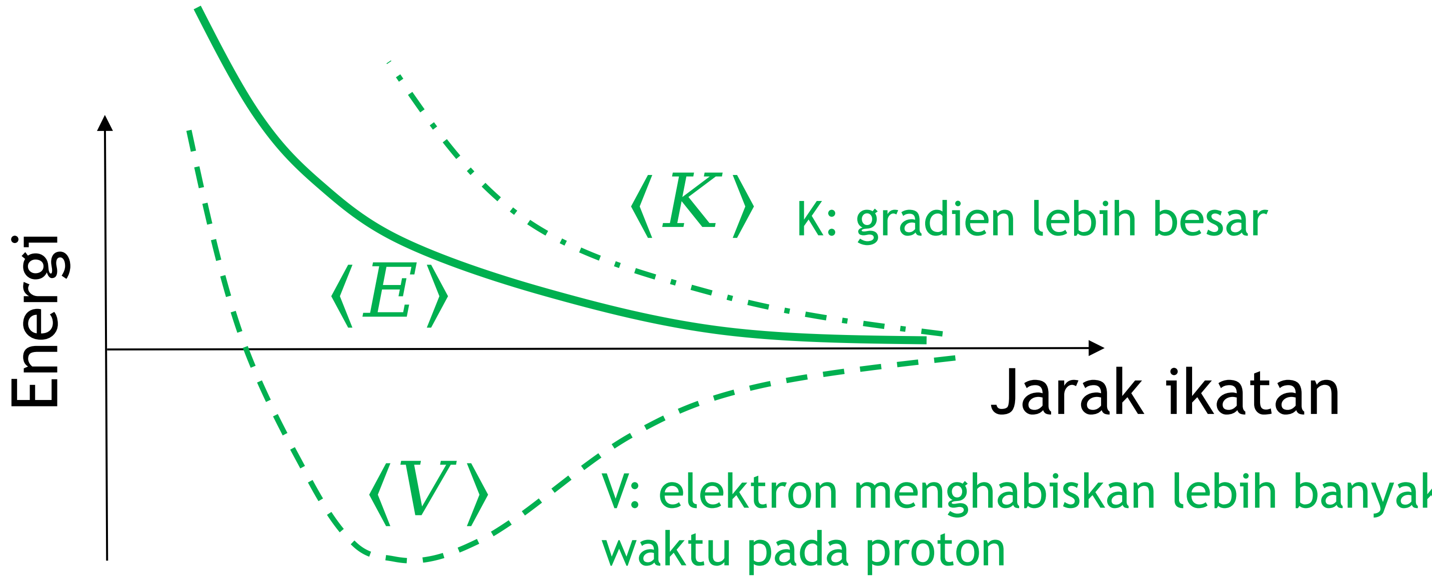
Simetris: $a_L = a_R$



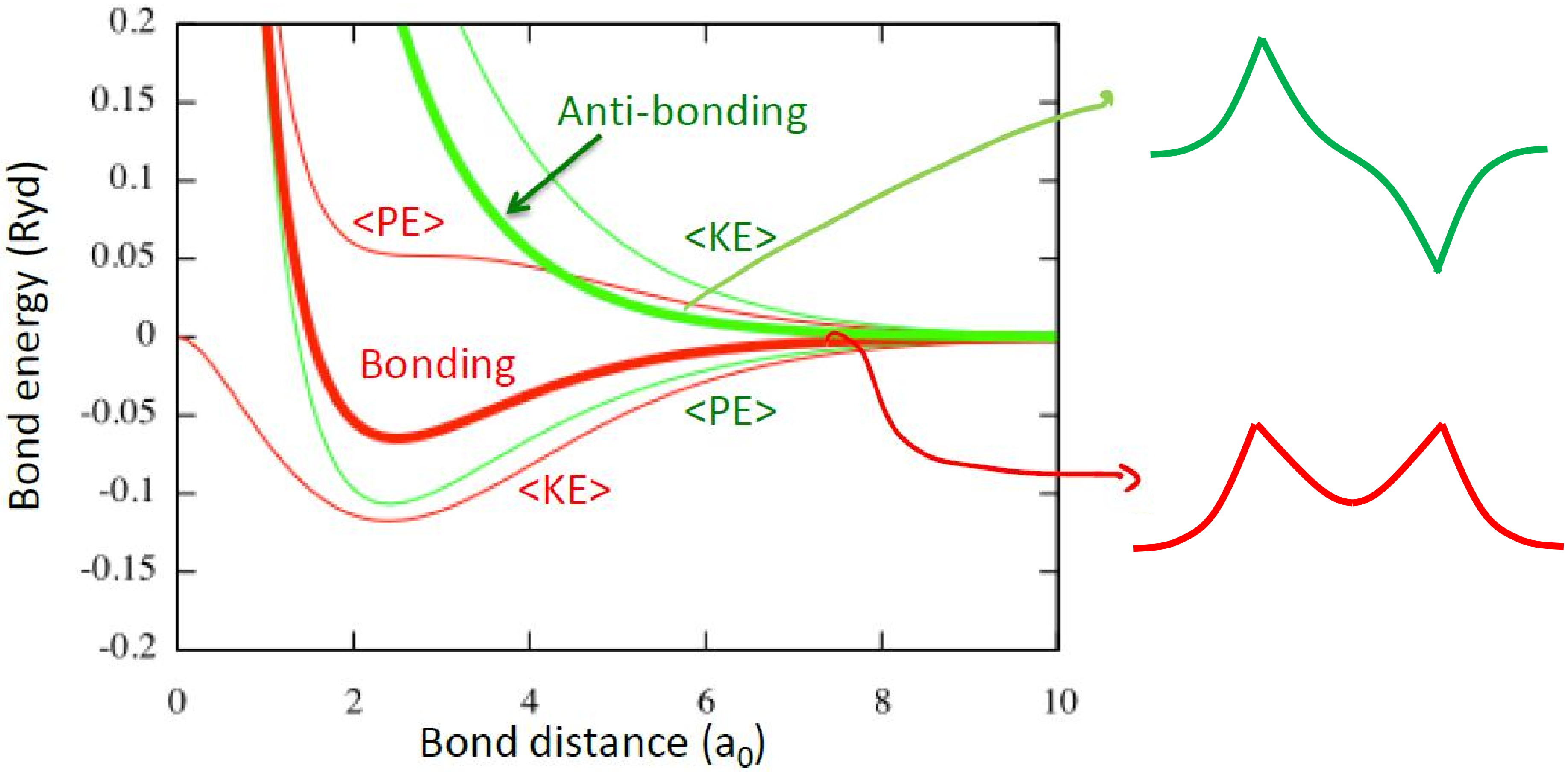


Antisimetris: $a_R = - a_L$





Rekapitulasi kontribusi energi



Ref: *The nature of the chemical bond*, William A. Goddard, III
http://authors.library.caltech.edu/25022/

Kuis #6

- Manakah pernyataan berikut ini yang benar?

(A) Energi kinetik dari keadaan ikatan lebih rendah dari anti-ikatan

(B) Energi potensial dari keadaan ikatan lebih rendah dari anti-ikatan

(C) Ikatan kovalen terbentuk karena elektron di tengah ikatan menarik dua ion bersamaan.

(D) Semua di atas benar.

Kuis #7

- Manakah fungsi gelombang yang asimetris dari pilihan berikut ini?

(A) $|\psi\rangle = |\psi_{\mathrm{L}}\rangle$

(B) $|\psi\rangle = |\psi_{\mathrm{R}}\rangle$

(C) $|\psi\rangle = \frac{1}{\sqrt{2}}(|\psi_{\mathrm{L}}\rangle + |\psi_{\mathrm{R}}\rangle)$

(D) $|\psi\rangle = \frac{1}{\sqrt{2}}(|\psi_{\mathrm{L}}\rangle - |\psi_{\mathrm{R}}\rangle)$

Aproksimasi Struktur Elektronik Molekul

Kombinasi linear orbital atom: $\Psi(x) = \sum_{i=1}^{N} C_i \varphi(x - \mathbf{R}_i)$

$\varphi(x - \mathbf{R}_i)$: Orbital atom pada $\mathbf{R} = \mathbf{R}_i$

Perhitungan energi:

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\sum_{i,j} C_i^* C_j H_{ij}}{\sum_{i,j} C_i^* C_j S_{ij}}$$

$S_{ij} = \langle \varphi_i | \varphi_j \rangle : \mathbf{S}$ (*Overlap matrix*)

$H_{ij} = \langle \varphi_i | H | \varphi_j \rangle : \mathbf{H}$ (*Hamiltonian matrix*)

$$\sum_j C_j H_{ij} - E \sum_j C_j S_{ij} = 0, \ (i = 1, \cdots, N)$$

Overlap matrix $\mathbf{S} = \{S_{ij}\}$, $\mathbf{C} = {}^t\{C_j\}$

$$(\mathbf{H} - E\mathbf{S})\mathbf{C} = 0$$

Hamiltonian matrix $\mathbf{H} = \{H_{ij}\}$

$$\mathbf{C} \neq 0 \Leftrightarrow \boxed{\det(\mathbf{H} - E\mathbf{S}) = 0}$$

Secular equation

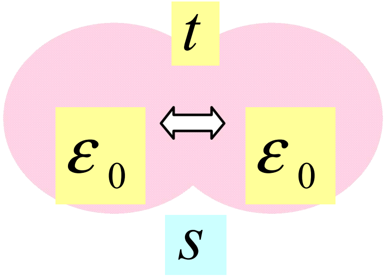
Langkah perhitungan

- Isi matriks H dan S
- Pecahkan determinan persamaan sekuler
- Dapatkan nilai eigen dan vektor eigen
- Susun keadaan elektron dari energi terendah

Fungsi eigen dibentuk dari koefisien vektor eigen

$$\Psi_k(x) = \sum_{i=1}^{N} C_{ik}\varphi(x - \mathbf{R}_i)$$

Contoh molekul hidrogen: 2 elektron 2 orbital 1s

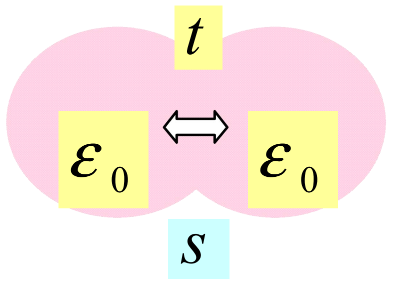


$$\Psi(x) = C_1\varphi_1 + C_2\varphi_2$$

$$H = \begin{pmatrix} \varepsilon_0 & t \\ t & \varepsilon_0 \end{pmatrix}, \; S = \begin{pmatrix} 1 & s \\ s & 1 \end{pmatrix}$$

$$\det(H - ES) = \begin{vmatrix} \varepsilon_0 - E & t - sE \\ t - sE & \varepsilon_0 - E \end{vmatrix} = 0$$

Hasil u/ molekul hidrogen



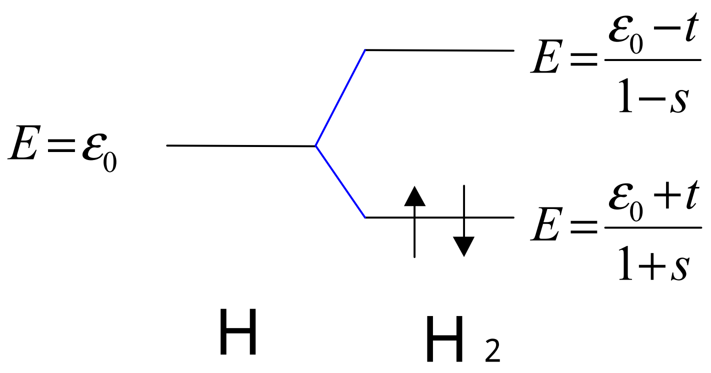
$$\det(H - ES) = \begin{vmatrix} \varepsilon_0 - E & t - sE \\ t - sE & \varepsilon_0 - E \end{vmatrix} = 0$$

$$t < 0,\ s > 0$$

$$\Psi(x) = C_1\varphi_1 + C_2\varphi_2$$

Energi: $E = \dfrac{\varepsilon_0 \pm t}{1 \pm s}$

Vektor eigen: $\begin{pmatrix} \varepsilon_0 - E & t - sE \\ t - sE & \varepsilon_0 - E \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0$



Masukkan nilai setiap energi ke persamaan matriks

$$E = \frac{\varepsilon_0 + t}{1 + s} \Leftrightarrow C_1 : C_2 = 1 : 1$$

$$E = \frac{\varepsilon_0 - t}{1 - s} \Leftrightarrow C_1 : C_2 = 1 : -1$$

Normalisasi

$$|\psi|^2 = 1 \Leftrightarrow |C_1|^2 + 2|C_1||C_2|s + |C_2|^2 = 1$$

$$\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = \frac{1}{\sqrt{2(1+s)}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}, \frac{1}{\sqrt{2(1-s)}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

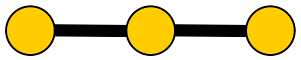
Bagaimana dengan molekul 3 atom?

Contoh: Li_3 (basis 3 elektron 2s)

Aproksimasi t < 0 dan s = 0 **S** = **I** (matriks identitas)

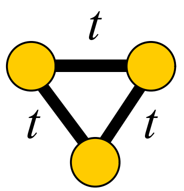
- Rantai linear

$$H = \begin{pmatrix} 0 & t & 0 \\ t & 0 & t \\ 0 & t & 0 \end{pmatrix}$$



- Segitiga

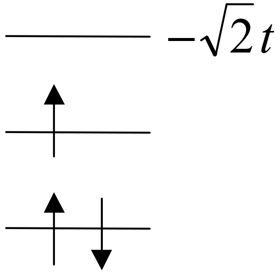
$$H = \begin{pmatrix} 0 & t & t \\ t & 0 & t \\ t & t & 0 \end{pmatrix}$$



$$E = 0, \pm\sqrt{2}\,t$$

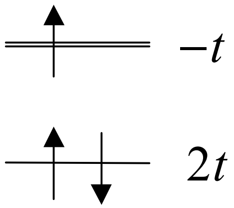
$$\Leftarrow \det(H - EI) = 0 \Rightarrow$$

$$E = 2t, -t, -t$$



Manakah struktur yang lebih stabil?

Cari energi total yang lebih rendah!



Kuis #8

- Asumsikan $t < 0$, konfigurasi paling stabil dari molekul Li_3 adalah:

(A) Rantai linear dengan energi total $2\sqrt{2}t$

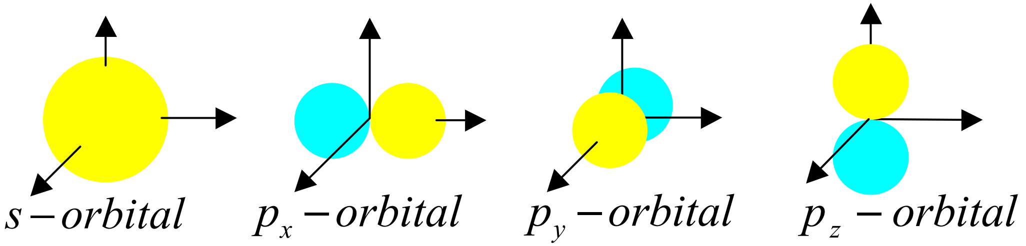
(B) Segitiga dengan energi total 0

(C) Segitiga dengan energi total $3t$

(D) Rantai linear dengan energi total $-\sqrt{2}t$

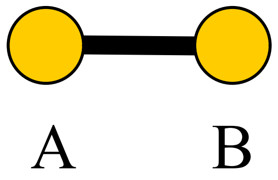
Lebih banyak orbital atom?

$\mathrm{C}: 1s^2, 2s^2, 2p^2$



Contoh: C_2 Setiap atom menyumbang basis: 2 elektron 2s dan 2 elektron 2p

Total orbital basis = 8



Matriks 8x8 yang dapat dijadikan blok 2x2

$$H = \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}$$

$$H = \begin{pmatrix} 0 & 0 & 0 & 0 & t_{2s} & t_{sp} & 0 & 0 \\ 0 & \varepsilon & 0 & 0 & -t_{sp} & -t_{pp\sigma} & 0 & 0 \\ 0 & 0 & \varepsilon & 0 & 0 & 0 & t_{pp\pi} & 0 \\ 0 & 0 & 0 & \varepsilon & 0 & 0 & 0 & t_{pp\pi} \\ t_{2s} & -t_{sp} & 0 & 0 & 0 & 0 & 0 & 0 \\ t_{sp} & -t_{pp\sigma} & 0 & 0 & 0 & \varepsilon & 0 & 0 \\ 0 & 0 & t_{pp\pi} & 0 & 0 & 0 & \varepsilon & 0 \\ 0 & 0 & 0 & t_{pp\pi} & 0 & 0 & 0 & \varepsilon \end{pmatrix}$$

$$H_{AA} = H_{BB} = \begin{array}{c} \begin{array}{cccc} s & p_x & p_y & p_z \end{array} \\ \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \varepsilon & 0 & 0 \\ 0 & 0 & \varepsilon & 0 \\ 0 & 0 & 0 & \varepsilon \end{pmatrix} \end{array} \begin{array}{c} s \\ p_x \\ p_y \\ p_z \end{array}$$

$$H_{AB} = {}^{t}H_{BA} = \begin{array}{c} \begin{array}{cccc} s & p_x & p_y & p_z \end{array} \\ \begin{pmatrix} t_{2s} & t_{sp} & 0 & 0 \\ -t_{sp} & -t_{pp\sigma} & 0 & 0 \\ 0 & 0 & t_{pp\pi} & 0 \\ 0 & 0 & 0 & t_{pp\pi} \end{pmatrix} \end{array} \begin{array}{c} s \\ p_x \\ p_y \\ p_z \end{array}$$

Komponen diagonal $E_{2p} - E_{2s} \equiv \varepsilon$