Teori Kuantum untuk Material
Bagian #01-1

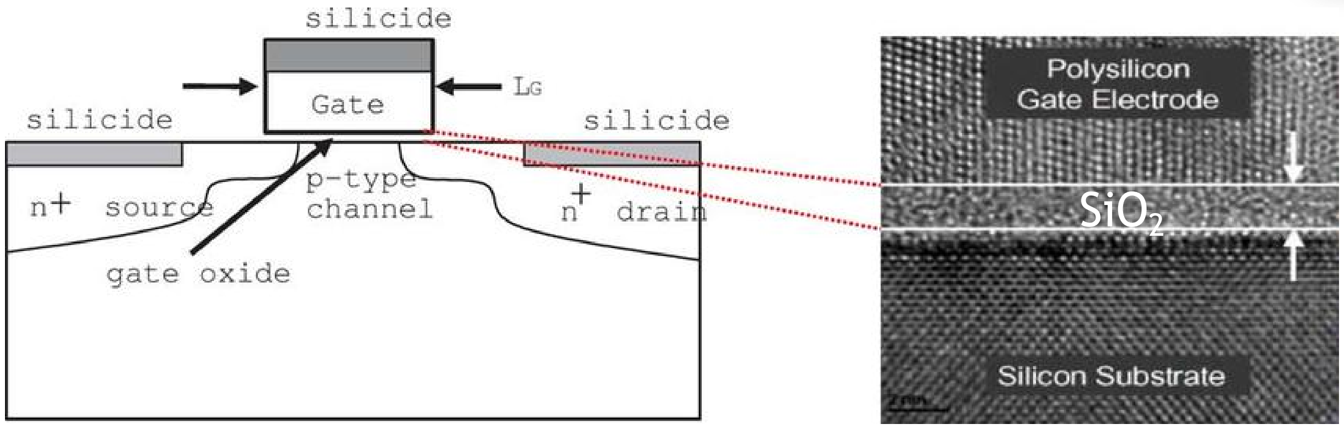
- Tujuan Pembelajaran
- Sifat/Properti Material
- Peran Sains Prediktif

Ahmad **Ridwan** Tresna **Nugraha**
Pusat Riset Fisika Kuantum, Badan Riset & Inovasi Nasional

Material di mana-mana!

Material rangka/struktur

Bahan obat



S. J. Bae et al., IEEE Trans Reliab. **56**, 392-400

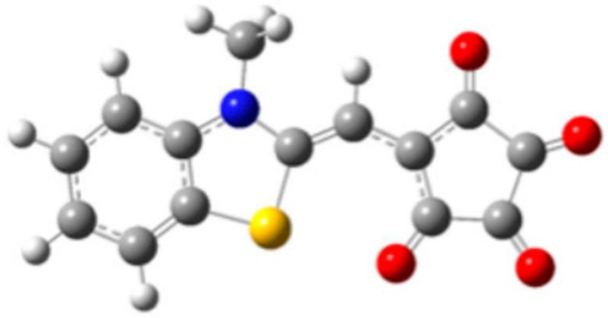
Mikroelektronika/
Nanoelektronika

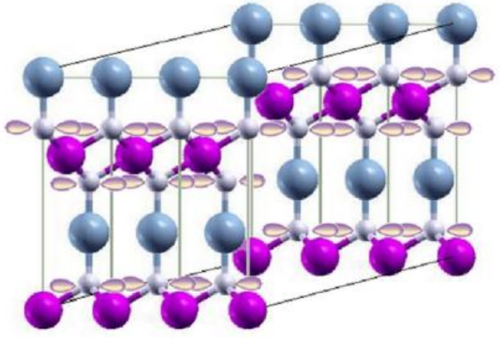
Tujuan pembelajaran

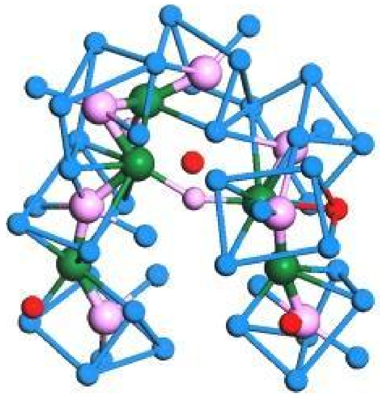
Dalam kuliah “Teori Kuantum untuk Material” ini,
kita akan belajar:

- **Fisika fundamental** yang membangun **material** pada **skala atom**
- **Hubungan** proses fisis **mikroskopis** dan dunia **makroskopis**
- **Perangkat lunak** untuk **prediksi sifat**/properti **material**

Beragam bentuk material



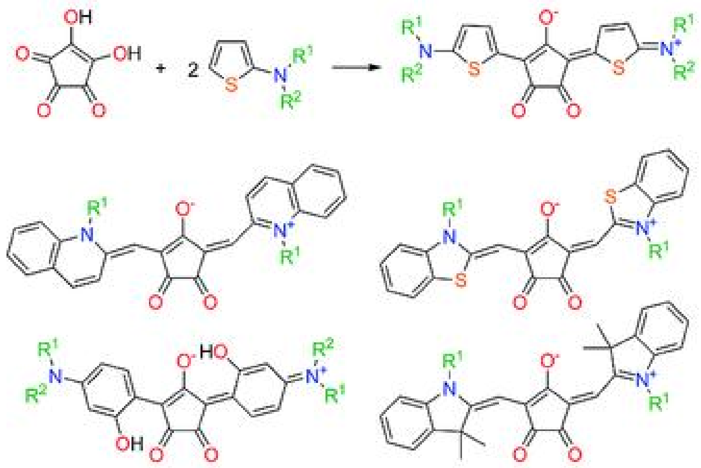


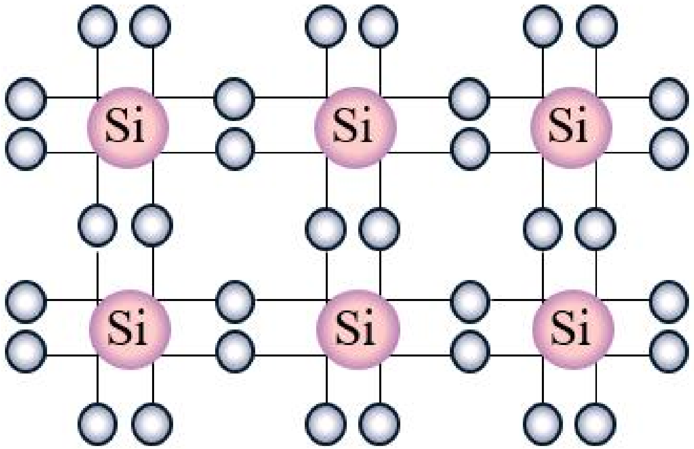


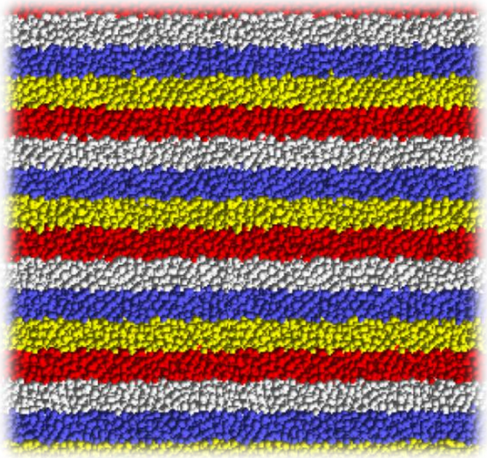
Material molekuler

Keramik & Semikonduktor

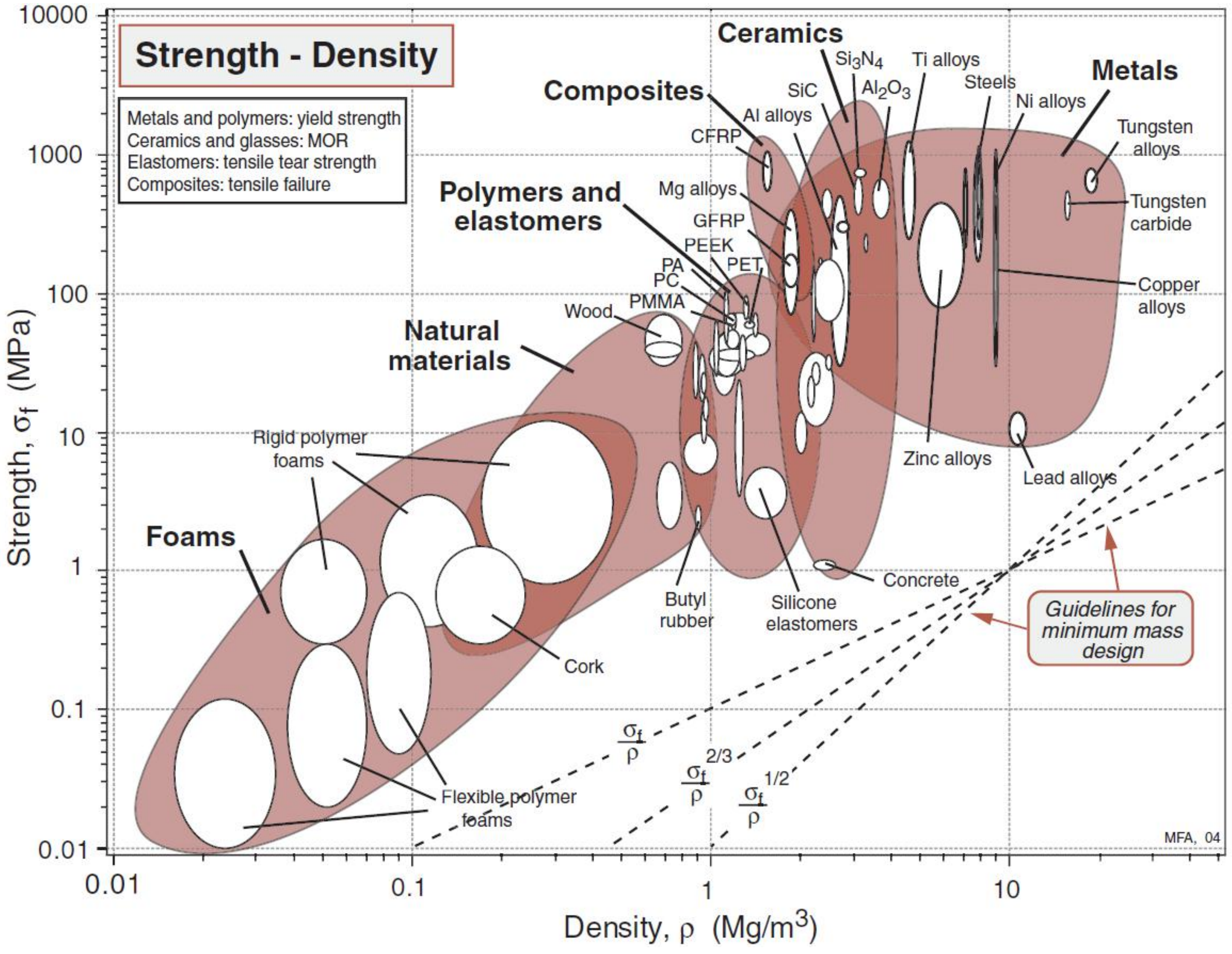
Logam/Metal

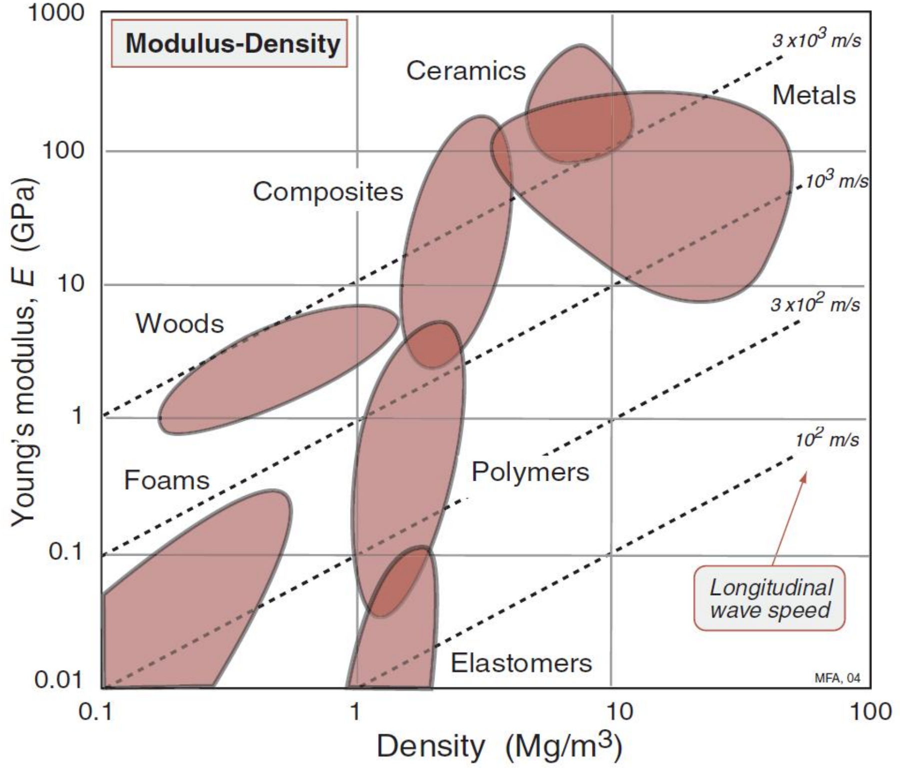






Sifat/properti material





M. F. Ashby, *Materials Selection in Mechanical Design*, 3rd edition (2005)

Sains prediktif untuk material

Quantum Mechanics of Many-Electron Systems.

By P. A. M. Dirac, St. John's College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received March 12, 1929.)

§ 1. *Introduction.*

The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give high-speed particles are involved, and are therefor sideration of atomic and molecular structure and in which it is, indeed, usually sufficiently accur variation of mass with velocity and assumes only various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

Already before the arrival of quantum mechanics there existed a theory of atomic structure, based on Bohr's ideas of quantised orbits, which was fairly successful in a wide field. To get agreement with experiment it was found necessary to introduce the spin of the electron, giving a doubling in the number of orbits of an electron in an atom. With the help of this spin and Pauli's exclusion principle, a satisfactory theory of multiplet terms was obtained when one made the additional assumption that the electrons in an atom all set them

It seemed to show that there were large forces coupling the spin vectors of the electrons in an atom, much larger forces than could be accounted for as due to the interaction of the magnetic moments of the electrons. The position was thus that there was empirical evidence in favour of these large forces, but that their theoretical nature was quite unknown.

Hukum-hukum dasar yang diperlukan untuk melakukan prosedur matematis dari sebagian besar ilmu fisika dan seluruh ilmu kimia telah diketahui sepenuhnya. Kesulitannya hanya terletak pada kenyataan bahwa penerapan hukum-hukum ini sering memberikan persamaan yang terlalu rumit untuk dipecahkan.

P.A.M. Dirac, Proc. R. Soc. Lond. A, 123 (792), 714-733 (1929)

Fisika fundamental dan aproksimasinya

Dalam mekanika kuantum:

- **Sekumpulan atom** dapat direpresentasikan oleh **fungsi gelombang**
- **Evolusi fungsi gelombang** terhadap waktu dideskripsikan oleh **persamaan Schrödinger**

$$i\hbar \frac{d}{dt}\Psi(\mathbf{r},t) = H\Psi(\mathbf{r},t)$$

Terlalu rumit dipecahkan walau oleh superkomputer

Contoh pendekatan (aproksimasi):

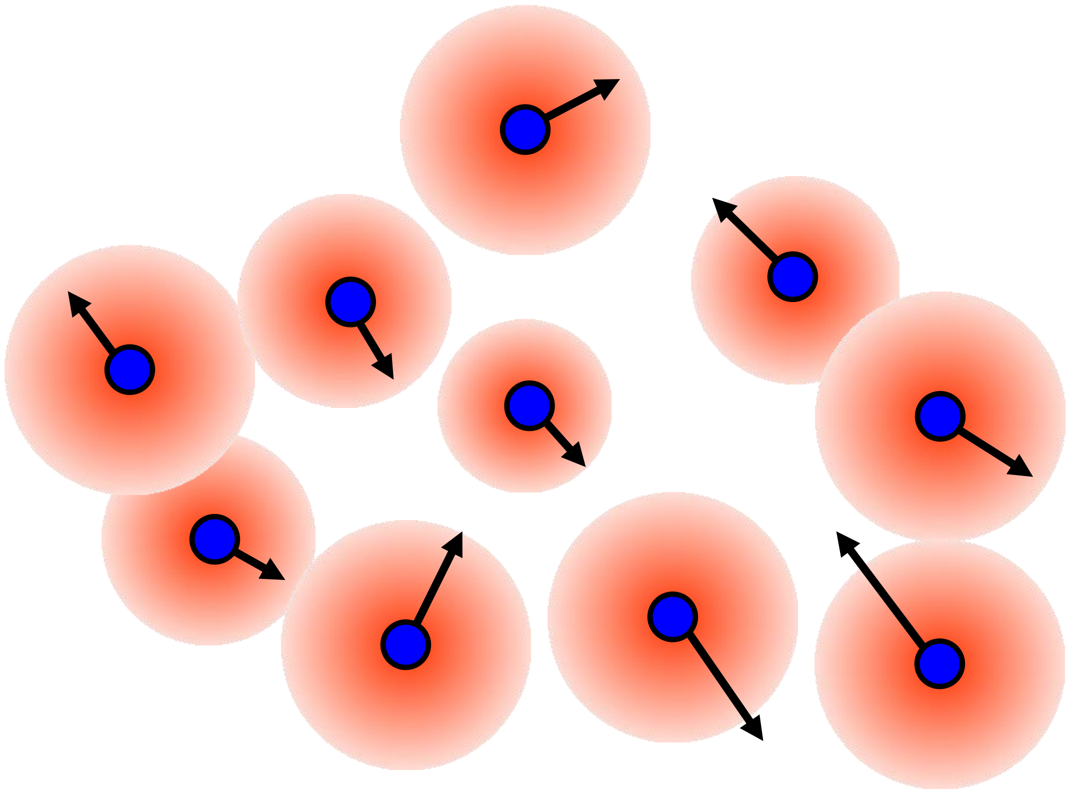
Elektron:
Pers. Schrödinger Bebas Waktu

$$H\psi = E\psi$$

Ion:
Mekanika Newton (klasik)

$$F = ma$$

Interaksi elektronik pada skala atom



Kondisi awal

$$\{\mathbf{R}_i\} \quad \{\mathbf{v}_i\}$$

Evolusi waktu

$$\dot{\mathbf{R}}_i = \mathbf{v}_i$$

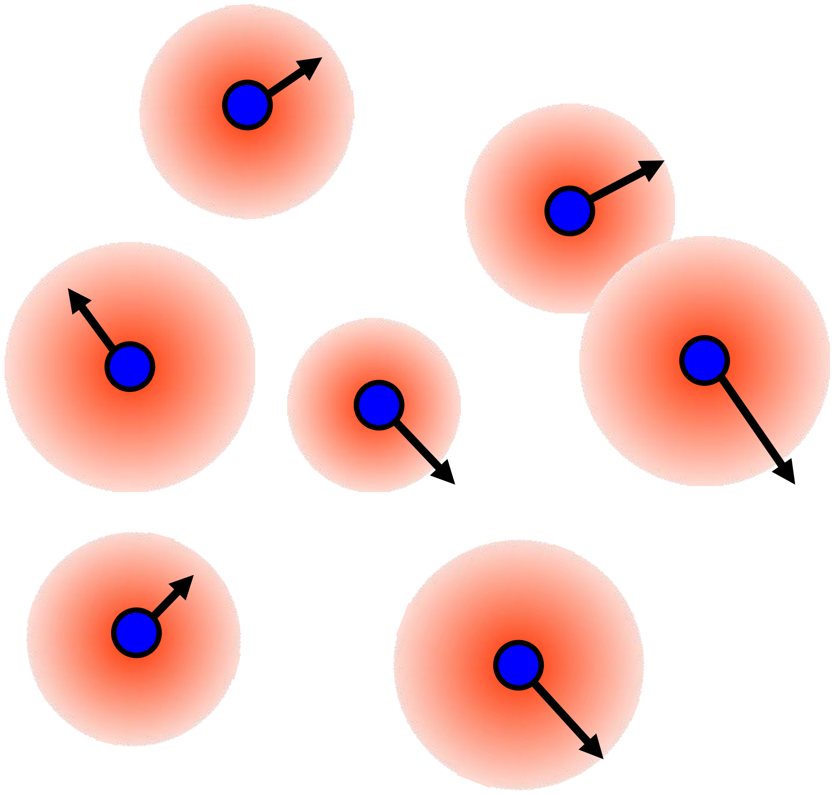
$$\dot{\mathbf{v}}_i = \frac{\mathbf{F}_i}{M_i}$$

Energi dan gaya

$$H\psi = E\psi$$

$$\mathbf{F}_i = -\nabla_{\mathbf{R}_i} E(\{\mathbf{R}_i\})$$

Dinamika molekuler



Kondisi awal

$$\{\mathbf{R}_i\} \quad \{\mathbf{v}_i\}$$

Hitung energi & gaya

$$H\psi = E\psi$$

$$\mathbf{F}_i = -\nabla_{\mathbf{R}_i} E$$

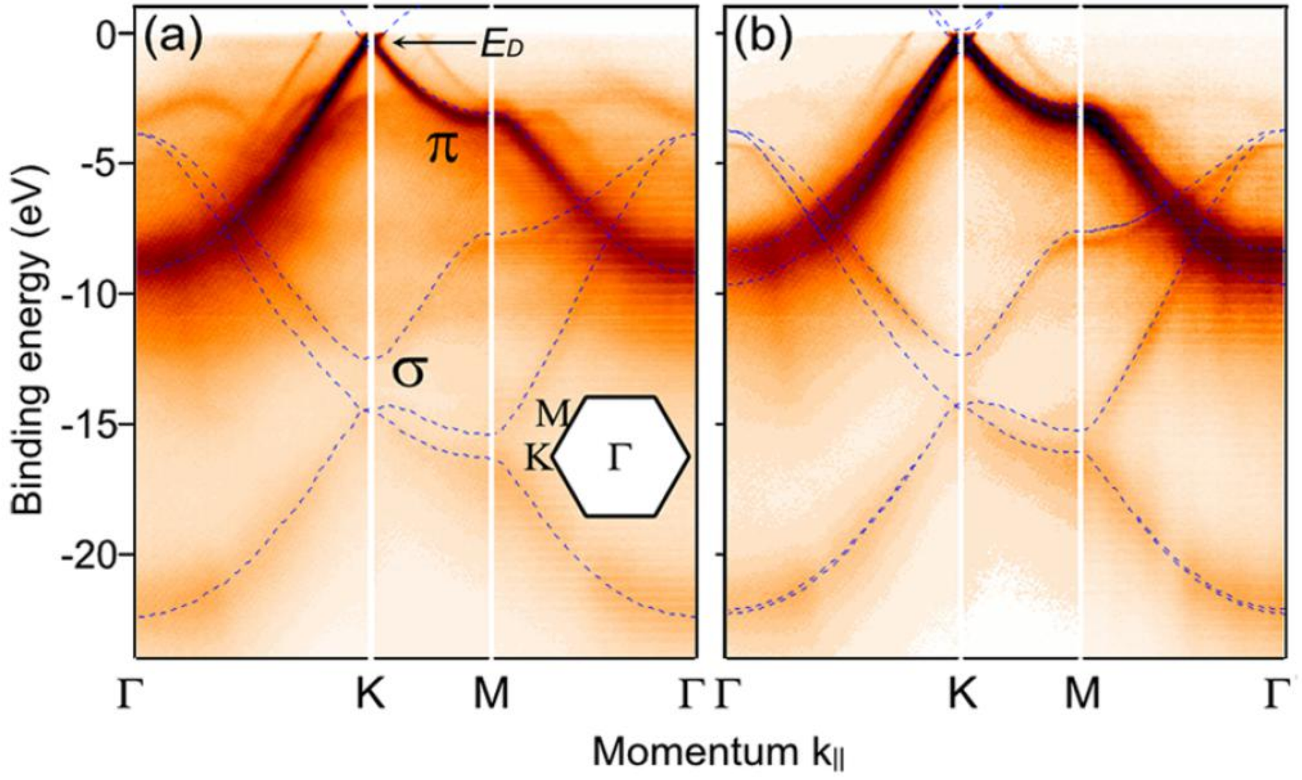
Integrasi pers. gerak

$$\mathbf{R}_i(t) \rightarrow \mathbf{R}_i(t+\Delta t)$$

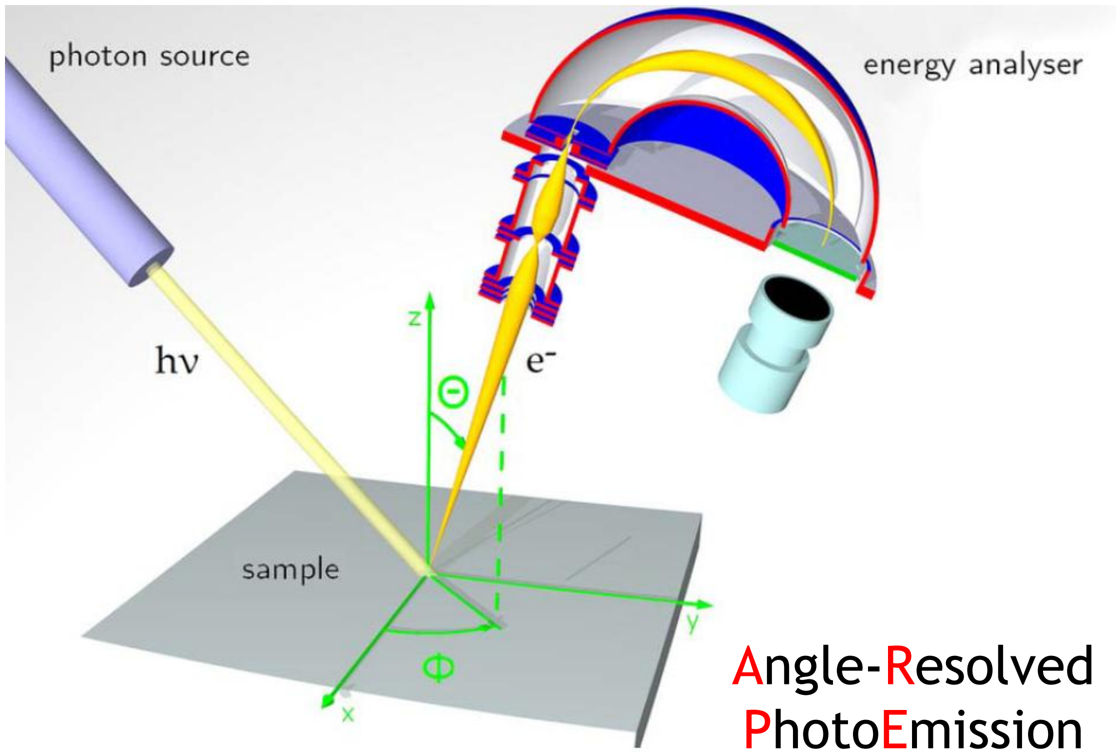
$$\mathbf{v}_i(t) \rightarrow \mathbf{v}_i(t+\Delta t)$$

Dunia mikroskopis dan makroskopis

Sifat elektronik material yang dihitung dari mekanika kuantum (dunia mikroskopis) mesti dapat teramati secara makroskopis, misalnya melalui eksperimen ARPES



T. Ohta et al., Phys. Rev. Lett. **98**, 206802 (2007)



Angle-Resolved PhotoEmission Spectroscopy

Perencanaan kuliah

EVALUASI:
- Kuis di kelas (15%?)
- Problem set di rumah (30%?)
- Ujian (25%?)
- Tugas besar (30%?)

GARIS BESAR MATERI:
- Mekanika Kuantum Dasar
- Struktur Atom, Molekul, Kristal
- Teori Fungsional Kerapatan (DFT)
- Sifat Fisis Material Berbasis DFT
- Aplikasi Teori Gangguan pada Material
- Density Matrix Approach
- dll.

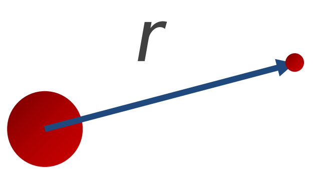
PERANGKAT LUNAK:
- Quantum ESPRESSO, Wannier90/WannierBerri, EPW
- Paket pemrograman dalam bahasa Python:
Paket pemrograman dalam bahasa Python
- Additional tools: VS Code, Git/GitHub

Teori Kuantum untuk Material
Bagian #01-2

- Urgensi mekanika kuantum
- Mekanika kuantum dasar untuk perhitungan struktur elektronik

Atom paling sederhana

Hidrogen:



Bagaimana jika kita perlakukan dengan mekanika klasik?

Keadaan sistem

(asumsi proton masif "fixed" dalam ruang)

- Posisi dan kecepatan elektron

$$\vec{r}(t) \qquad \vec{v}(t)$$

Energi

(kondisi setimbang → energi minimum)

- Potensial : $V(r) = \dfrac{Q_1 Q_2}{r} = -\dfrac{e^2}{|\vec{r}|}$ (satuan cgs)

- Kinetik : $K = \dfrac{1}{2} m|\vec{v}|^2 = \dfrac{|\vec{p}|^2}{2m}$

Momentum linear: $\vec{p} = m\vec{v}$

Atom hidrogen klasik

Hidrogen:

r

Elektron ($-e$)

Proton ($+e$)

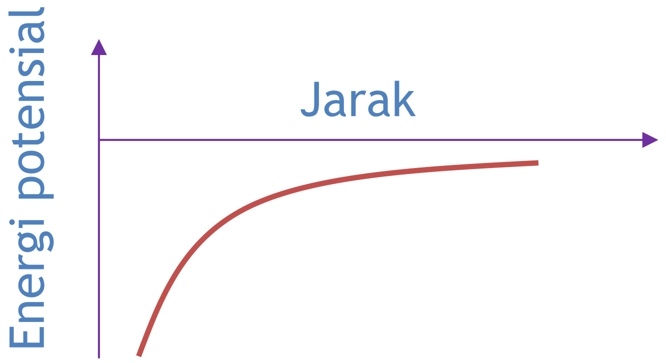
Pendekatan klasik:

$$E = K + V = \frac{|\vec{p}|^2}{2m} - \frac{e^2}{r}$$

Keadaan dengan energi minimum (kondisi setimbang)?

$$\min(K) \quad \rightarrow \quad \vec{p} = 0$$

$$\min(V) \quad \rightarrow \quad |\vec{r}| = 0$$

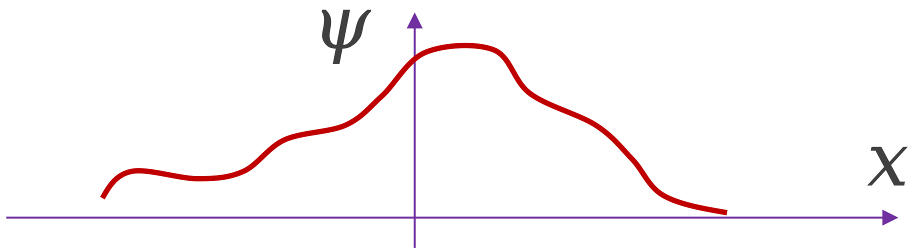


Keruntuhan atom!

Mekanika kuantum?

Keadaan sistem → Fungsi gelombang (fungsi dari posisi $\vec{r}$ yang menggambarkan peluang menemukan elektron pada posisi tsb)

$\psi(\vec{r})$



Besaran fisis yang diamati → operator

("*observables*") (objek matematis yang bekerja pada fungsi)

Posisi : $\mathbf{r}$ kalikan fungsi dengan $\vec{r}$

Momentum : $\mathbf{p} = \frac{\hbar}{i}\vec{\nabla} = \frac{\hbar}{i}\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$

operasi gradien

Mekanika kuantum?

Pengukuran eksperimen: nilai harap dari suatu operator

Integral pada seluruh ruang:

$$\langle O \rangle = \int \psi^*(\vec{r}) O \psi(\vec{r}) d^3r$$

$$d^3r = dx\,dy\,dz$$

Contoh pengukuran posisi:

$$\langle \mathbf{r} \rangle = \int \psi^*(\vec{r}) \mathbf{r} \psi(\vec{r}) d^3r = \int \vec{r} |\psi(\vec{r})|^2 d^3r$$

Contoh pengukuran momentum:

$$\langle \mathbf{p} \rangle = \int \psi^*(\vec{r}) \mathbf{p} \psi(\vec{r}) d^3r = \frac{\hbar}{i} \int \psi^*(\vec{r}) \vec{\nabla} \psi(\vec{r}) d^3r$$

Atom hidrogen kuantum

$$H = K + V$$

$$\langle H \rangle = \int \psi^*(\vec{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r} \right] \psi(\vec{r}) d^3r$$

$$= -\frac{\hbar^2}{2m} \int \psi^*(\vec{r}) \nabla^2 \psi(\vec{r}) d^3r - e^2 \int \frac{|\psi(\vec{r})|^2}{r} d^3r$$

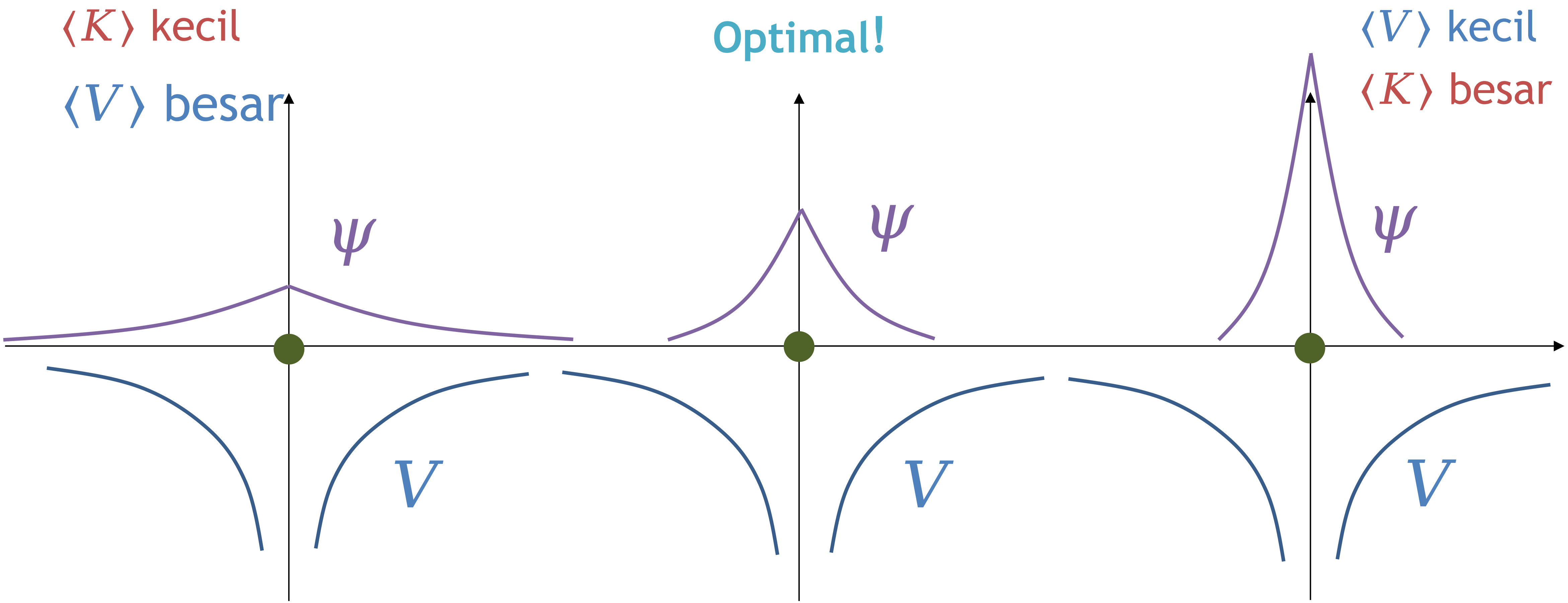
$$\langle K \rangle \qquad \qquad \langle V \rangle$$

Untuk meminimalkan energi:

- Kinetik : fungsi gelombang mulus $\rightarrow$ gradien kecil
- Potensial : $|\psi|^2$ lebih besar untuk $|\vec{r}|$ yang kecil

Atom hidrogen kuantum

$$\langle H \rangle = -\frac{\hbar^2}{2m}\int \psi^*(\vec{r})\nabla^2\psi(\vec{r})d^3r - e^2\int \frac{|\psi(\vec{r})|^2}{r}d^3r$$



Rangkuman peninjauan hidrogen

Mekanika klasik

Keadaan sistem:

$\vec{r}(t) \qquad \vec{p}(t)$

Energi: $E = \dfrac{p^2}{2m} - \dfrac{e^2}{r}$

Keadaan dasar (energi minimum):

$r = 0 \qquad E = -\infty$

Atom tidak eksis!

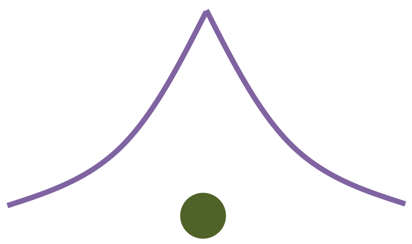
Mekanika klasik gagal → **Mekanika kuantum**

Keadaan sistem:

$\psi(\vec{r})$

Energi: $H = -\dfrac{\hbar^2}{2m}\nabla^2 - \dfrac{e^2}{r}$

Keadaan dasar: ukuran berhingga



Energi kinetik menstabilkan atom

Kuis #1

- Pernyataan manakah yang benar di bawah ini?

  (A) Gradien yang besar untuk fungsi gelombang memberikan energi kinetik yang besar

  (B) Fungsi gelombang elektron mengandung informasi posisi serta momentum elektron

  (C) Semua (A+B) benar.

Postulat mekanika kuantum

❶ Keadaan partikel ditentukan oleh fungsi gelombangnya

$\Psi(\vec{r}, t)$ Kita akan fokus pada sifat ekuilibrium
Fungsi gelombang bebas dari waktu $\Rightarrow$ $\psi(\vec{r})$

❷ "Observables" ↔ operator linear

Pengukuran direpresentasikan objek matematis yang bekerja pada fungsi gelombang

Posisi : $\vec{r}$

Momentum : $\vec{p} = \frac{\hbar}{i}\vec{\nabla} = \frac{\hbar}{i}\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$

Postulat mekanika kuantum

❸ Hasil rata-rata pengukuran diberikan oleh nilai harap operator

$$\langle O \rangle = \int \psi^*(\vec{r}) O \psi(\vec{r}) d^3r$$

Contoh:

$$\langle \vec{r} \rangle = \int \psi^*(\vec{r}) \vec{r} \psi(\vec{r}) d^3r = \int \vec{r} |\psi(\vec{r})|^2 d^3r$$

$|\psi(\vec{r})|^2$ Rapat probabilitas elektron berada pada volume d^3r di sekitar posisi r

Postulat mekanika kuantum

❹ Fungsi gelombang kondisi ekuilibrium diperoleh dari persamaan Schrödinger tak bergantung waktu:

$$H\psi(\vec{r}) = E\psi(\vec{r})$$

Permasalahan nilai eigen: $\mathbf{A}\mathbf{x} = \lambda\mathbf{x}$

Solusi: ψ_n , E_n

❺ Prinsip eksklusi Pauli

- Maksimum dua elektron per orbital
- Elektron-elektron pada satu orbital harus memiliki spin berlawanan

Operator Hamiltonian

- Hamiltonian *H* adalah operator untuk energi total sistem
- Dapat ditulis sebagai jumlah dua operator (kinetik + potensial)

Atom hidrogen

Energi kinetik

$$K = \frac{|\vec{p}|^2}{2m} = -\frac{\hbar^2}{2m}\vec{\nabla}\cdot\vec{\nabla} = -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

Energi potensial

$$V = -\frac{e^2}{|\vec{r}|}$$

Hamiltonian ala Born-Oppenheimer

(bisa diberlakukan tidak hanya untuk hidrogen)

- Setiap material adalah kumpulan elektron dan inti atom
  - N_e buah elektron pada posisi $\vec{r}_i$
  - N_n buah inti atom (nuklir) bermuatan Z_i pada posisi $\vec{R}_i$

- Pendekatan Born-Oppenheimer
  - Inti atom masif bersifat klasik dan tetap pada ruang

$$H = -\sum_{i=1}^{N_e} \frac{\hbar^2}{2m} \nabla_i^2 - \sum_i^{N_n} \sum_j^{N_e} \frac{e^2 Z_i}{|\vec{r}_j - \vec{R}_i|} + \sum_{i<j}^{N_n} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} + \sum_{i<j}^{N_e} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

K interaksi e-n interaksi n-n interaksi e-e

Sifat pers. Schrödinger

$$H\psi(\vec{r}) = E\psi(\vec{r})$$

permasalahan nilai eigen

$$\mathbf{A}\mathbf{x} = \lambda\mathbf{x}$$

$$E_n \qquad \psi_n(\vec{r})$$

sekelompok solusi

$$\lambda_n \qquad \vec{x}_n$$

Nilai eigen harus riil sehingga Hamiltonian bersifat hermitian

↓

Fungsi gelombang bersifat "ortonormal" satu dengan lainnya

$$\int_{-\infty}^{\infty} \psi_n(\vec{r})\psi_m(\vec{r})d^3r = \delta_{nm}$$

Matriks simetris memiliki nilai eigen riil

↓

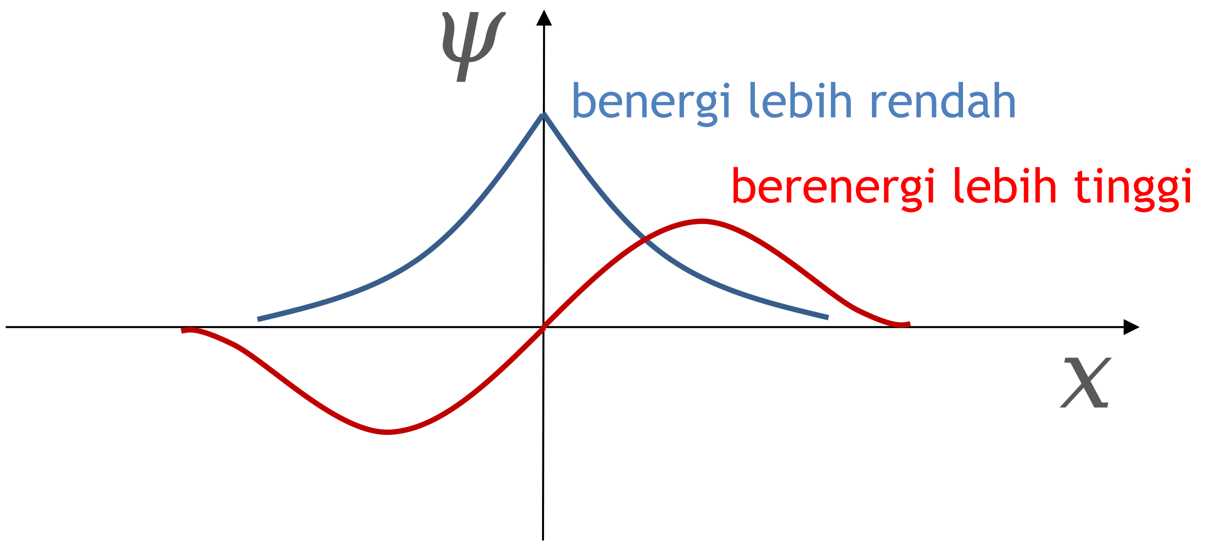
Vektor eigen bersifat "ortonormal" satu dengan lainnya

$$\vec{x}_n\vec{x}_m = \sum_{i=1}^{N} x_{n,i}x_{m,i} = \delta_{ij}$$

Teorema simpul fungsi gelombang

- Fungsi gelombang keadaan dasar (energi terendah) tidak memiliki simpul kecuali pada perbatasan domain

- Semakin banyak simpul dimiliki oleh suatu fungsi gelombang, semakin besar pula energinya



Kuis #2

- Manakah formula di bawah ini yang merepresentasikan operator Hamiltonian atom hidrogen dalam pendekatan Born-Oppenheimer?

(A) $-\frac{\hbar^2}{2m}\nabla - \frac{e^2}{|\vec{r}|}$

(B) $-\frac{\hbar^2}{2m}\nabla^2 - \frac{2e^2}{|\vec{r}|}$

(C) $\frac{\hbar^2}{2m}\nabla^2 - \frac{2e^2}{|\vec{r}|}$

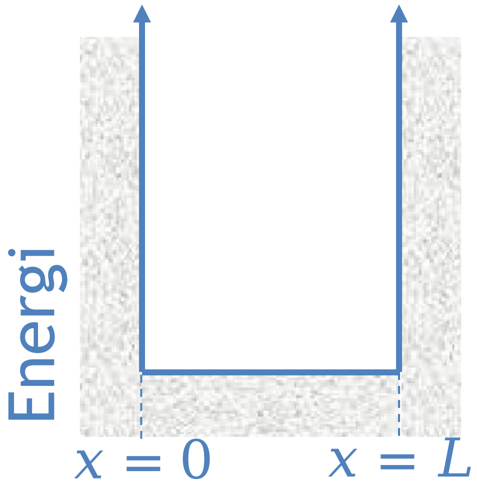
(D) $-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{|\vec{r}|}$

Teori Kuantum untuk Material Bagian #01-3

- Pemecahan Persamaan Schrödinger
  - Sumur Potensial Sederhana
  - Kuantisasi dan Sifat Optik

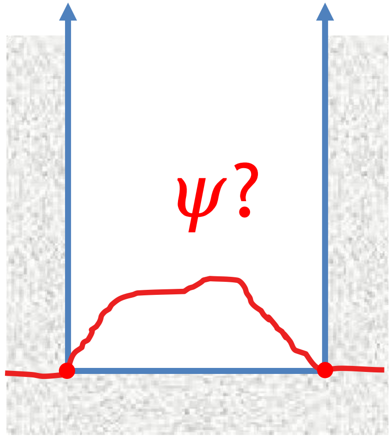
Sumur Potensial Tak Hingga

“Partikel dalam kotak atau sumur kuantum”



Persamaan Schrödinger bebas waktu:

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi(x) = E\psi(x)$$



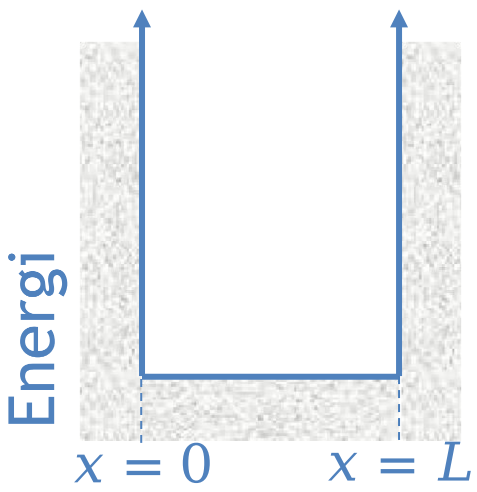
Persamaan Schrödinger di dalam sumur:

$x = [0, L] \rightarrow V = 0$

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} = E\psi(x)$$

Apa solusinya?

Syarat Batas & Tebakan Solusi



Apa permasalahan kita?

Solusi memenuhi : $-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi(x)$

dan syarat batas : $\begin{cases} \psi(0) = 0 \\ \psi(L) = 0 \end{cases}$

Coba-coba fungsi: $\psi(x) = A\sin(kx)$

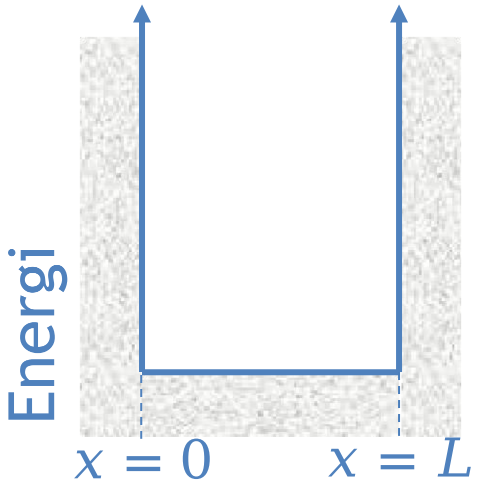
$$\frac{\partial\psi}{\partial x} = kA\cos(kx) \quad \& \quad \frac{\partial^2\psi}{\partial x^2} = -k^2 A\sin(kx)$$

$$\Rightarrow \frac{\hbar^2}{2m}k^2 \cancel{A\sin(kx)} = E\cancel{A\sin(kx)}$$

$$\boxed{E = \frac{\hbar^2 k^2}{2m}}$$

k dicari dari syarat batas

Syarat Batas & Tebakan Solusi



Tebakan $\psi(x) = A\sin(kx)$ $\quad E = \dfrac{\hbar^2 k^2}{2m}$

Syarat batas : $\psi(0) = 0 \rightarrow A\sin(k.0) = 0$

$\psi(L) = 0 \rightarrow A\sin(k.L) = 0$

$kL = n\pi \quad ; \quad n = 1,\ 2,\ 3,\ \ldots \Rightarrow k_n = \dfrac{n\pi}{L}$

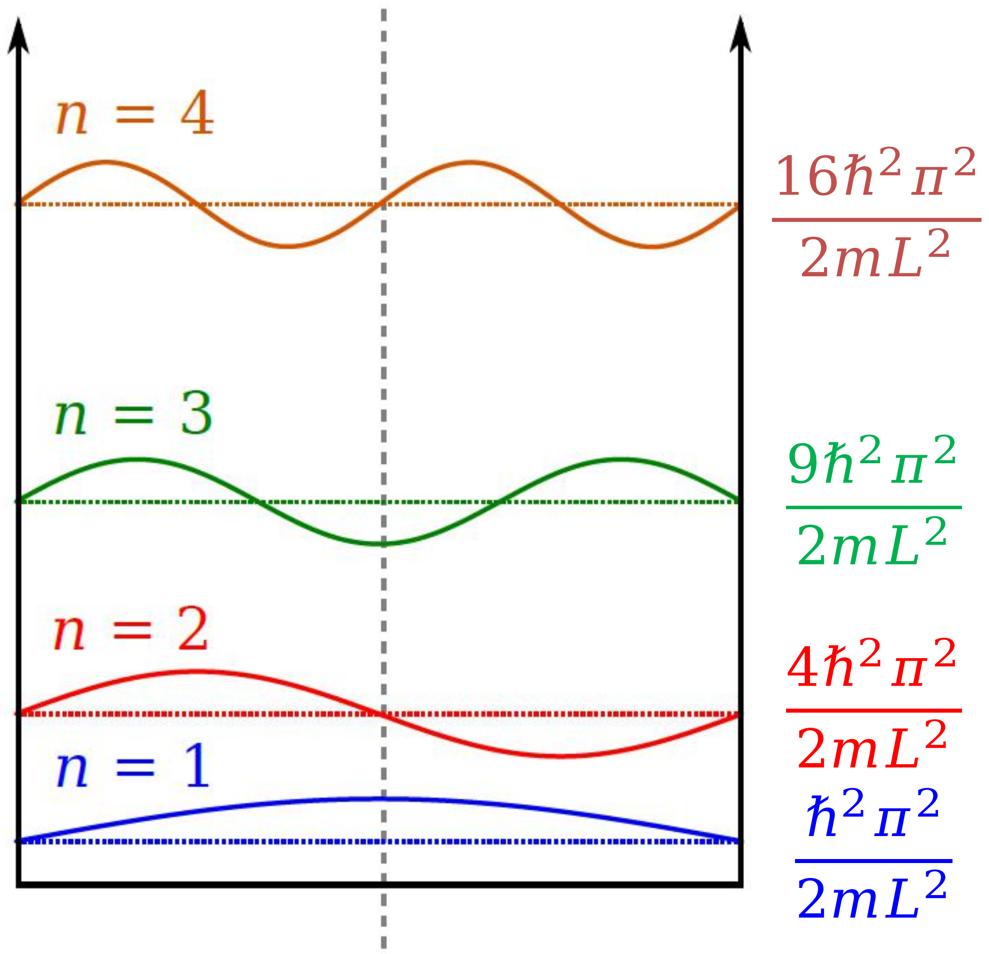
Fungsi gelombang:

$$\psi_n(x) = A\sin\left(\frac{n\pi}{L}x\right)$$

Energi:

$$E_n = \frac{n^2\hbar^2\pi^2}{2mL^2}$$

Kuantisasi pada Sumur Potensial

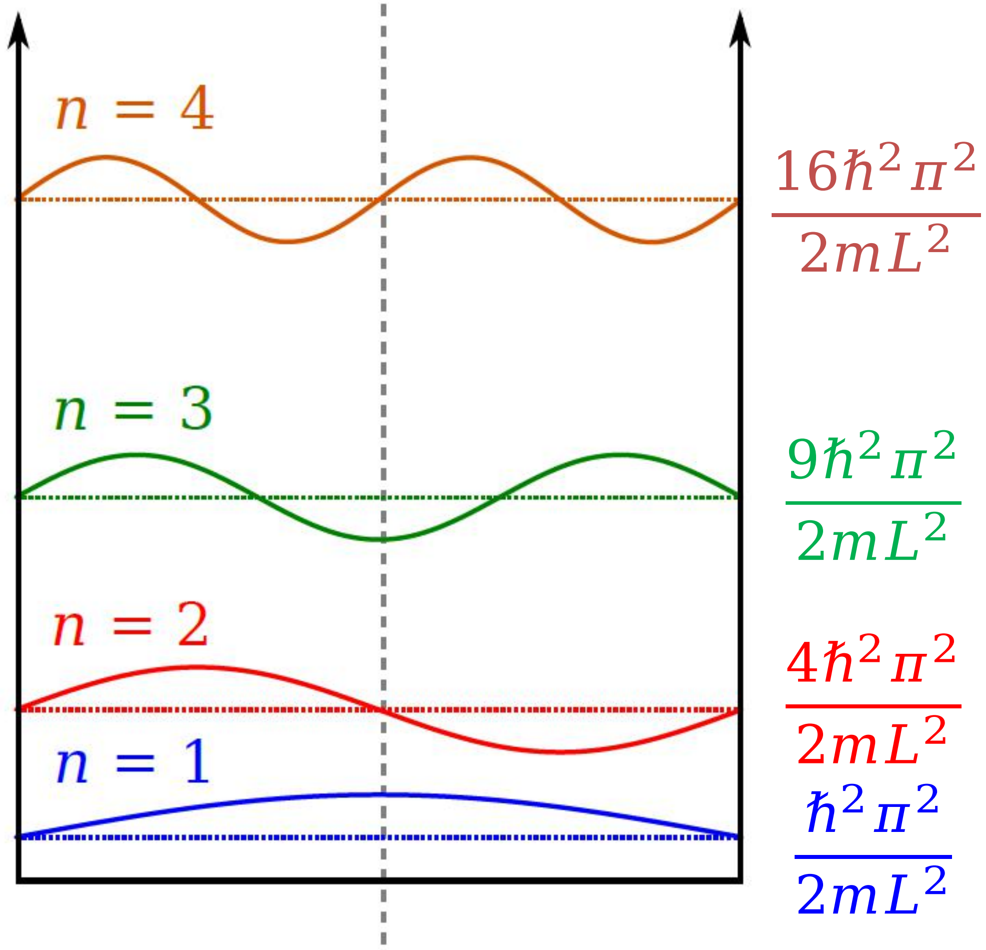


- Hanya **nilai tertentu** dari *k* dan energi yang diizinkan ada (**terkuantisasi**)
- Energi keadaan dasar **tidaklah sama dengan nol** (prinsip ketidakpastian)
- Semakin bergelombang suatu fungsi gelombang, semakin tinggi pula energinya*

(*ingat energi kinetik berbanding lurus gradient fungsi gelombang kuadrat)

Sifat Optik Sumur Potensial

Sifat optik ditentukan kemampuan penyerapan/pemancaran foton



$$E_\omega = \hbar\omega = h\nu$$

$$c = \lambda\nu = \lambda\frac{\omega}{2\pi}$$

Absorpsi (penyerapan):

Foton hanya dapat diserap jika ia membawa energi yang dibutuhkan untuk mendorong elektron ke keadaan tereksitasi

Emisi (pemancaran):

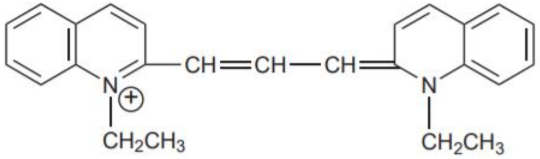
Elektron tereksitasi dapat turun ke keadaan energi lebih rendah dengan memancarkan foton berfrekuensi sebesar selisih energi elektron pada keadaan akhir dan awal

Contoh Molekul Model Sumur Kuantum

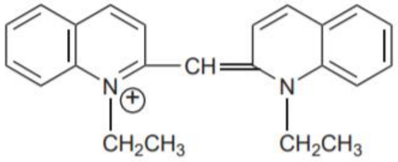
Visible Spectra of Conjugated Dyes: Integrating Quantum Chemical Concepts with Experimental Data

George M. Shalhoub
Department of Chemistry & Biochemistry, La Salle University, Philadelphia, PA 19141

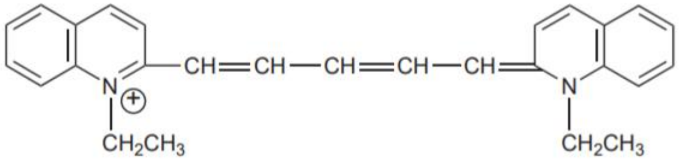
J. Chem. Educ. 74, 1317 (1997)



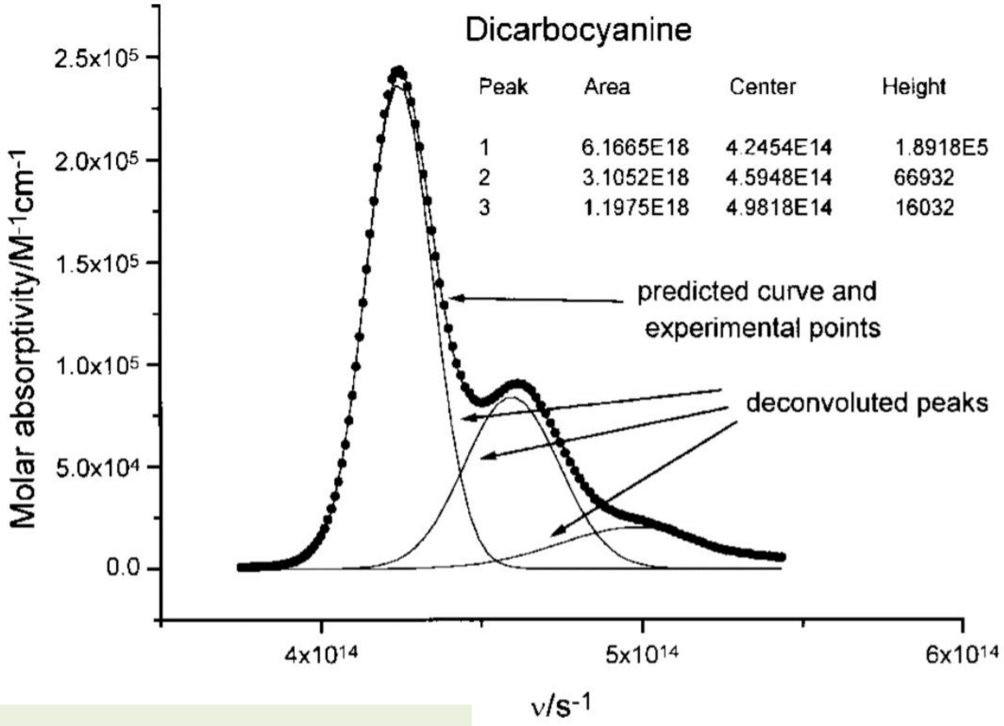
Pinacyanol Chloride MW = 388.94



1,1'-Diethyl-2,2' cyanine Iodide MW = 454.36



1,1'-Diethyl-2,2'-dicarbocyanine Iodide MW = 506.43



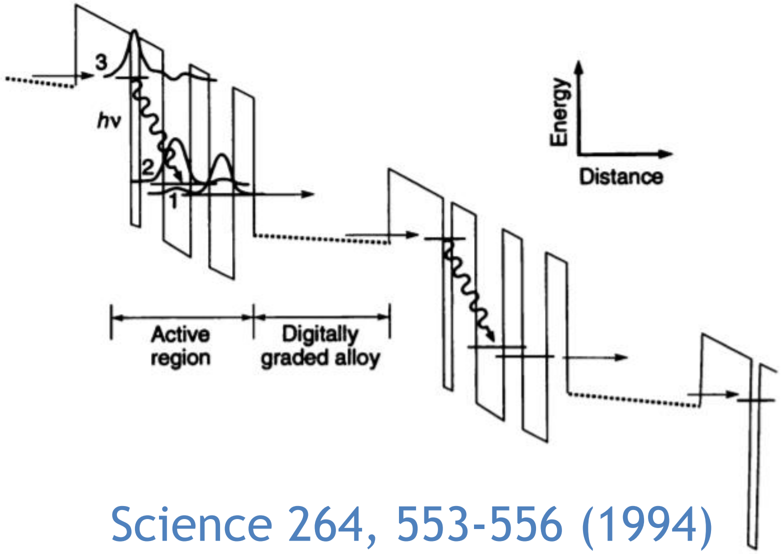
$$\Delta E = \frac{\hbar^2 \pi^2}{2mL^2}(n'^2 - n^2) = \hbar\omega = h\nu$$

Pengurungan Kuantum

Quantum Cascade Laser

Jerome Faist, Federico Capasso,* Deborah L. Sivco, Carlo Sirtori, Albert L. Hutchinson, Alfred Y. Cho

A semiconductor injection laser that differs in a fundamental way from diode lasers has been demonstrated. It is built out of quantum semiconductor structures that were grown by molecular beam epitaxy and designed by band structure engineering. Electrons streaming down a potential staircase sequentially emit photons at the steps. The steps consist of coupled quantum wells in which population inversion between discrete conduction band excited states is achieved by control of tunneling. A strong narrowing of the emission spectrum, above threshold, provides direct evidence of laser action at a wavelength of 4.2 micrometers with peak powers in excess of 8 milliwatts in pulsed operation. In quantum cascade lasers, the wavelength, entirely determined by quantum confinement, can be tailored from the mid-infrared to the submillimeter wave region in the same heterostructure material.

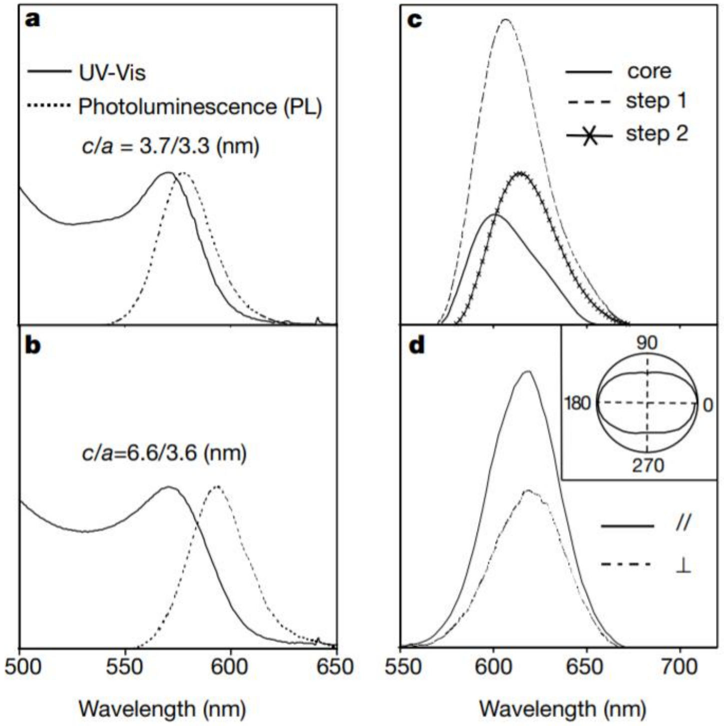


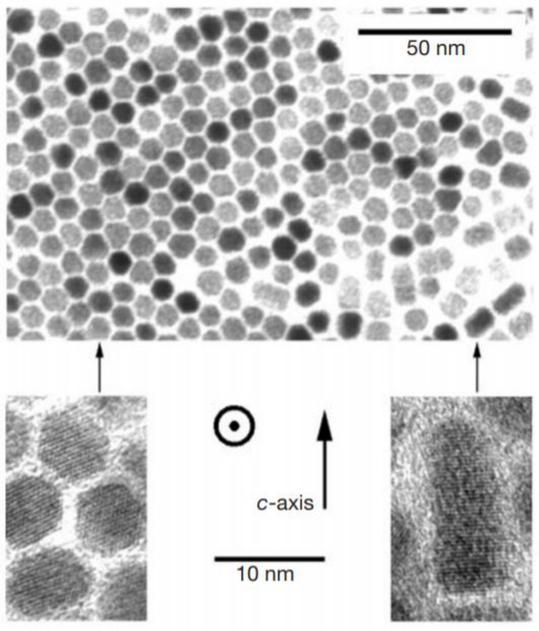
Science 264, 553-556 (1994)

Shape control of CdSe nanocrystals

Xiaogang Peng*, Liberato Manna, Weidong Yang, Juanita Wickham, Erik Scher, Andreas Kadavanich & A. P. Alivisatos

Department of Chemistry, University of California at Berkeley, and Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA





Nature 404, 59–61 (2000)

Kuis #3

- Manakah pernyataan berikut ini yang benar tentang sumur potensial tak hingga? (pilih jawaban terbaik)

(A) Energi keadaan dasar tidak bernilai nol sebagai akibat prinsip ketidakpastian

(B) Energi keadaan dasar berkurang dengan bertambahnya panjang sumur.

(C) Probabilitas menemukan elektron di luar sumur adalah nol.

(D) Semua di atas sudah benar.