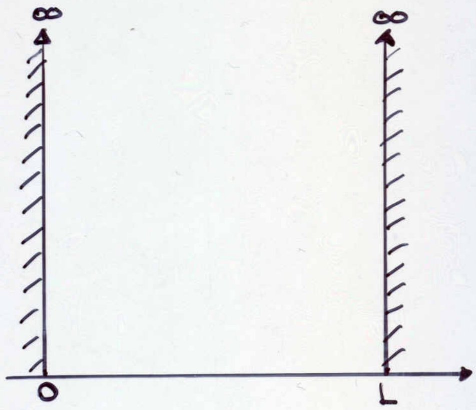
Σωμάτιο σε κουτί

Απειρόβαθο πηγάδι δυναμικού

$$V(x)=\begin{cases}0, & 0<x<L\\ \infty, & x\geq L,\ x\leq 0\end{cases}$$



εξ. Schrödinger $H\psi=E\psi \Rightarrow$

$$-\frac{\hbar^2}{2m}\psi''+V(x)\psi=E\psi \xRightarrow{\times\left(-\frac{2m}{\hbar^2}\right)} \psi''=\Big[\underbrace{\frac{2m}{\hbar^2}V(x)}_{\equiv v(x)}-\underbrace{\frac{2m}{\hbar^2}E}_{\equiv\epsilon}\Big]\psi \Rightarrow \psi''=\left[v(x)-\epsilon\right]\psi$$

A) μέσα στο κουτί $0<x<L \xRightarrow{V(x)=0} \psi''=-\epsilon\psi \Rightarrow \psi''=-k^2\psi \Rightarrow \psi''+k^2\psi=0$

$\epsilon>0 \Rightarrow \epsilon\equiv k^2$

ΔΕ: $\psi''+k^2\psi=0$

δοκιμάζω $\psi=e^{\rho x} \Rightarrow \psi''=\rho^2e^{\rho x}$ $\Big\}\Rightarrow \rho^2e^{\rho x}+k^2e^{\rho x}=0 \Rightarrow e^{\rho x}(\rho^2+k^2)=0 \Rightarrow$

ΧΕ: $\rho^2+k^2=0 \Rightarrow \rho=\pm ik$

$\Rightarrow \psi=c_1e^{ikx}+c_2e^{-ikx} \Rightarrow \psi=A\sin kx+B\cos kx$

B) έξω απ'το κουτί $x\geq L$, $x\leq 0$ $\psi(x)=0$

Γ) Συνοριακές συνθήκες $\psi(0)=\psi(L)=0$ $\Big\}\Rightarrow$

$\psi(0)=0 \Rightarrow B=0$

$\psi(L)=0 \Rightarrow A\sin kL=0 \Rightarrow kL=n\pi \ : n=1,2,\dots$ $\Big\}$ $\boxed{\psi_n=A\sin\frac{n\pi}{L}x}$

$$\epsilon=k^2=\frac{n^2\pi^2}{L^2}=\frac{2m}{\hbar^2}E \Rightarrow E=\boxed{E_n=\underbrace{\frac{\hbar^2\pi^2}{2mL^2}}_{\equiv E_1}n^2}=E_1n^2$$

Δ) Κανονικοποίηση $\int_{-\infty}^{+\infty}|\psi(x)|^2dx=1$

$$\Rightarrow A^2\int_0^L\sin^2kx\,dx=A^2\int_0^L\frac{1}{2}(1-\cos 2kx)\,dx=\frac{A^2}{2}\int_0^L dx-\frac{A^2}{2}\int_0^L\cos 2kx\,dx=$$

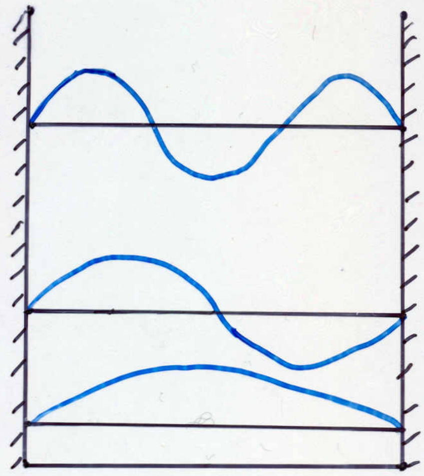
$$=\frac{A^2L}{2}-\frac{A^2}{4k}\int_0^L\cos 2kx\,d(2kx)=\frac{A^2L}{2}-\frac{A^2}{4k}\sin 2kx\Big|_0^L=\frac{A^2L}{2}=1 \Rightarrow A=\sqrt{\frac{2}{L}} \Rightarrow$$

$\sin 0=0$
$\sin 2kL=\sin 2n\pi=0$

$$\boxed{\psi_n=\sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x}$$

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2}\, n^2 \qquad n = 1, 2, \ldots$$

$$\psi_n = \sqrt{\frac{2}{L}} \sin\frac{n\pi}{L}x$$



Φυσική Ανάλυση Αποτελεσμάτων

1. κυματοσυναρτήσεις εναλλάξ άρτιες - περιττές

2. κόμβοι κυματοσυναρτήσεων

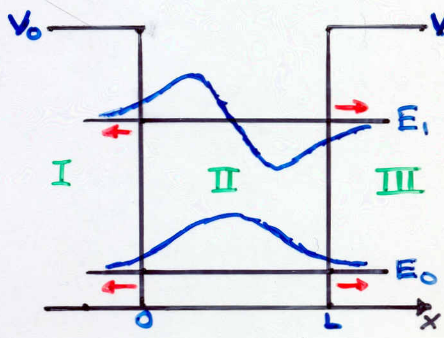
3. $E_1 \neq 0$ Ενέργεια Μηδενικού Σημείου

4. κλασσικό όριο $\left.\begin{matrix} \hbar \to 0 \\ m \to \infty \end{matrix}\right\} \Rightarrow E_1 \to 0$

   ισχυρό κβαντικό όριο $\left.\begin{matrix} L \to 0 \\ m \to 0 \end{matrix}\right\} \Rightarrow E_1 \to \infty$

5. Τετραγωνικό πηγάδι δυναμικού

   διείσδυση σε κλασσικά απαγορευμένη περιοχή



II : όπως απειρόβαθο

I, III: $\left.\begin{matrix} \dfrac{d^2\psi}{dx^2} = \underbrace{\dfrac{2m(V_0 - E)}{\hbar^2}}_{c^2}\psi \\ V_0 > E \Rightarrow \end{matrix}\right\} \Rightarrow \dfrac{d^2\psi}{dx^2} = c^2\psi$

$\Rightarrow \psi = Ae^{cx} + Be^{-cx}$

ψ: τετραγωνικά ολοκληρώσιμη

$\int_{-\infty}^{+\infty} |\psi(x)|^2 dx < \infty$

$\psi \underset{x\to\infty}{\to} 0$: δέσμια κατάσταση

$$\left.\right\} \quad \psi_I = Ae^{cx}, \quad \psi_{III} = Be^{-cx}, \quad \psi_{II} = F\sin(kx) + G\cos(kx)$$

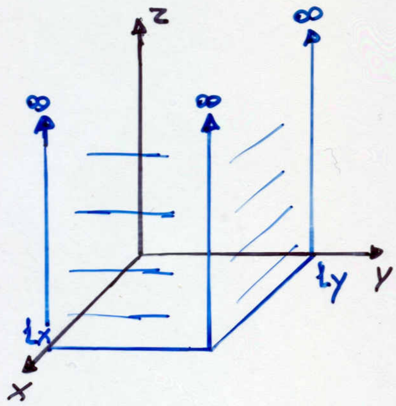
ΣΣ

$x=0$: $\psi_I = \psi_{II}$, $\dfrac{d\psi_I}{dx} = \dfrac{d\psi_{II}}{dx}$

$x=L$: $\psi_{II} = \psi_{III}$, $\dfrac{d\psi_{II}}{dx} = \dfrac{d\psi_{III}}{dx}$

$$E_n = \frac{E_n^{(\infty)}}{(1+g)^2}, \quad g = \frac{1}{2\sqrt{V_0}\,L}$$

Απειρόβαθο Πηγάδι 2-D



$$V(x)=0 \quad \begin{cases} 0<x<\ell_x \\ 0<y<\ell_y \end{cases}$$

- $H\Psi = E\Psi \Rightarrow \dfrac{-\hbar^2}{2m}\left[\dfrac{\partial^2\Psi(x,y)}{\partial x^2} + \dfrac{\partial^2\Psi(x,y)}{\partial y^2}\right] = E\Psi(x,y)$

- Διαχωρισμός Μεταβλητών $\psi(x,y) = X(x)\cdot Y(y)$

$$\text{ΘΕ} \mapsto \frac{-\hbar^2}{2m}\left[X''Y + Y''X\right] = E\cdot X\cdot Y \Rightarrow$$

$$\left.\underbrace{\frac{-\hbar^2}{2m}\frac{X''}{X}}_{f(x)} - \underbrace{\frac{\hbar^2}{2m}\frac{Y''}{Y}}_{g(y)} = E \;\right\} \Rightarrow \begin{array}{l} \dfrac{-\hbar^2}{2m}\dfrac{X''}{X} = \text{σταθ} = E_x \\ \dfrac{-\hbar^2}{2m}\dfrac{Y''}{X} = \text{σταθ} = E_y \end{array} \quad , E = E_x + E_y$$

$$\Rightarrow \begin{cases} X = \left(\dfrac{2}{\ell_x}\right)^{\frac{1}{2}} \sin\left(\dfrac{n_x\pi x}{\ell_x}\right) , & E_x = \dfrac{h^2 n_x^2}{8m\ell_x^2} \quad , n_x = 1,2,\ldots \\ Y = \left(\dfrac{2}{\ell_y}\right)^{\frac{1}{2}} \sin\left(\dfrac{n_y\pi y}{\ell_y}\right) , & E_y = \dfrac{h^2 n_y^2}{8m\ell_y^2} \quad , n_y = 1,2,\ldots \end{cases}$$

απειρόβαθο πηγάδι 1-D

$$\boxed{\begin{array}{l} \Rightarrow \Psi = \left(\dfrac{4}{\ell_x\ell_y}\right)^{\frac{1}{2}} \sin\left(\dfrac{n_x\pi x}{\ell_x}\right)\sin\left(\dfrac{n_y\pi y}{\ell_y}\right) \\ \Rightarrow E = \dfrac{h^2}{8m}\left(\dfrac{n_x^2}{\ell_x^2} + \dfrac{n_y^2}{\ell_y^2}\right) \qquad \begin{array}{l} n_x = 1,2,\ldots \\ n_y = 1,2,\ldots \end{array} \end{array}}$$

για τετραγωνικό πηγάδι $\Rightarrow \ell_x = \ell_y = L \Rightarrow E_{n_x n_y} = \dfrac{h^2}{8m\ell^2}(n_x^2 + n_y^2)$

να βρεθούν $E_{12}, E_{21}, \Psi_{12}, \Psi_{21}$:

$$E_{12} = \frac{5h^2}{8m\ell^2}$$

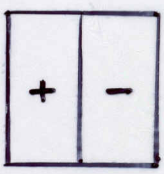
$$\Psi_{12} = \left(\frac{2}{\ell}\right)\sin\left(\frac{\pi x}{\ell}\right)\sin\left(\frac{2\pi y}{\ell}\right)$$

$$E_{21} = \frac{5h^2}{8m\ell^2}$$

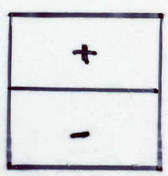
$$\Psi_{21} = \left(\frac{2}{\ell}\right)\sin\left(\frac{2\pi x}{\ell}\right)\sin\left(\frac{\pi y}{\ell}\right)$$

$E_{12} = E_{21}$, $\Psi_{12} \neq \Psi_{21}$

"εκφυλισμός"



Ψ_{21}



Ψ_{12}

15.

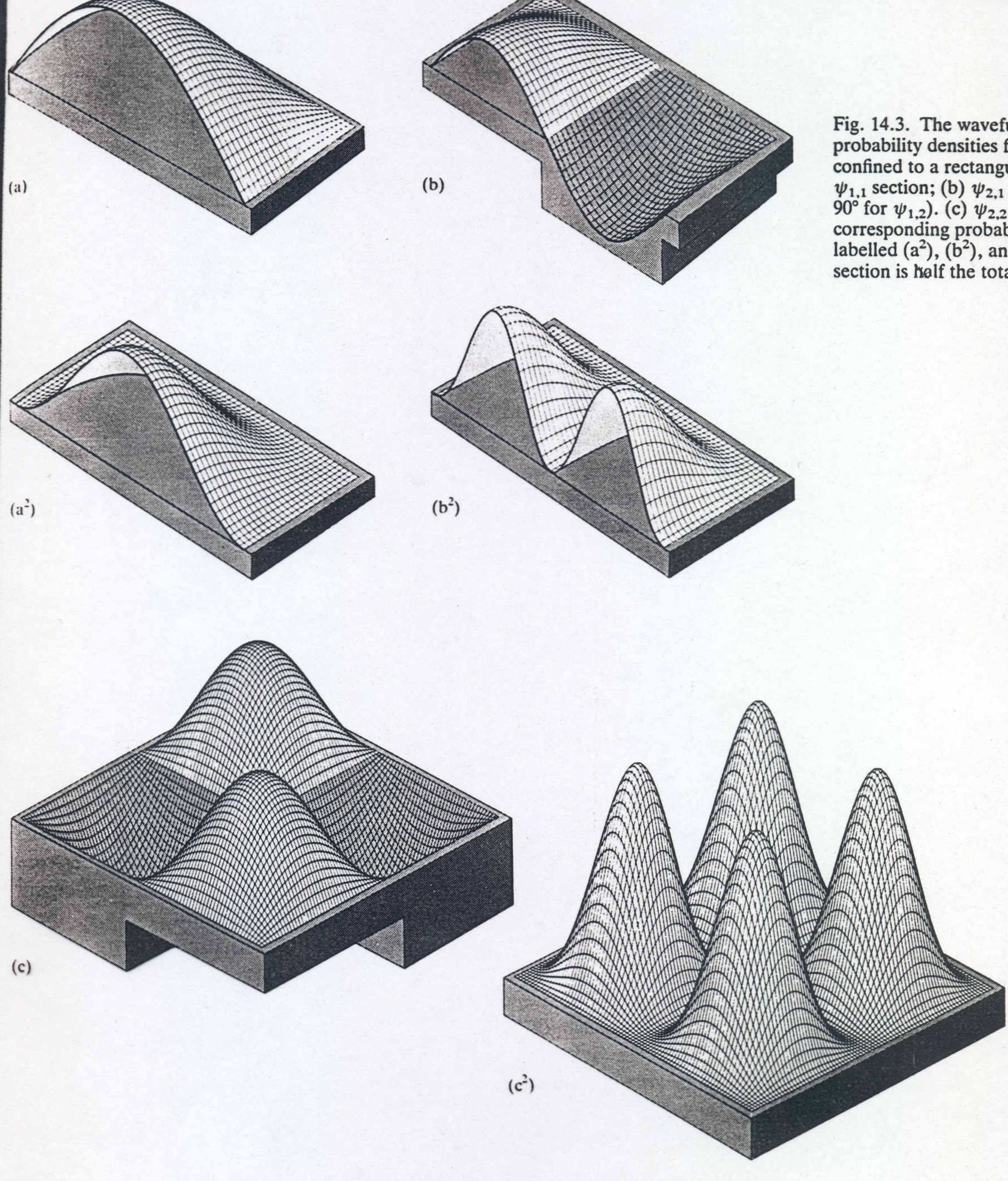


Fig. 14.3. The wavefunctions and probability densities for a particle confined to a rectangular surface. (a) $\psi_{1,1}$ section; (b) $\psi_{2,1}$ section (rotate by 90° for $\psi_{1,2}$). (c) $\psi_{2,2}$. The corresponding probability densities are labelled (a^2), (b^2), and (c^2). Each section is half the total function.

The three-dimensional case, of a particle in an actual box, can be treated in the same way, and the wavefunctions have another factor (for the z-dependence), and the energy has an additional term.

An interesting feature of the solutions is obtained when the plane surface is square, when $L_1 = L$ and $L_2 = L$. Then

$$\psi_{n_1,n_2} = (2/L)\sin(n_1\pi x/L)\sin(n_2\pi y/L),$$
$$E_{n_1,n_2} = \{n_1^2 + n_2^2\}(h^2/8mL^2).$$

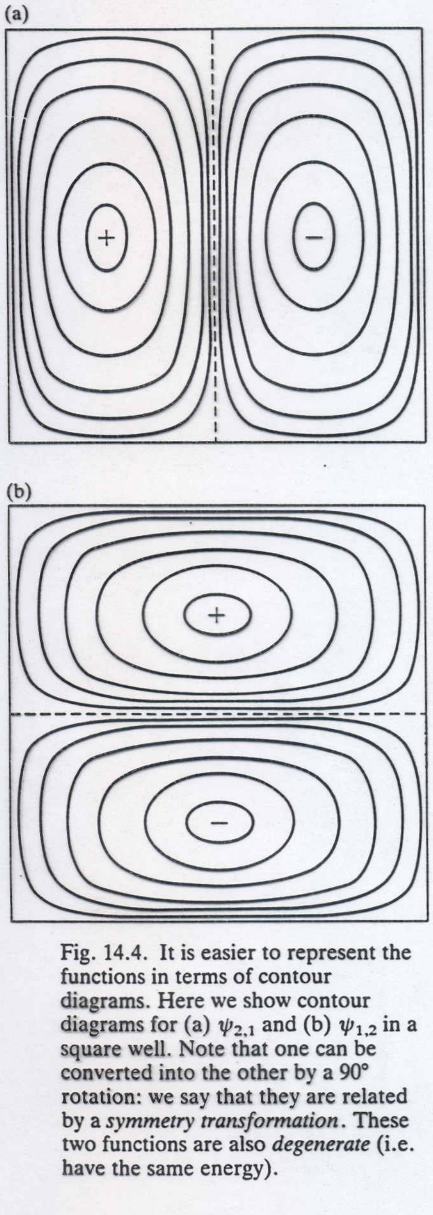


Fig. 14.4. It is easier to represent the functions in terms of contour diagrams. Here we show contour diagrams for (a) $\psi_{2,1}$ and (b) $\psi_{1,2}$ in a square well. Note that one can be converted into the other by a 90° rotation: we say that they are related by a *symmetry transformation*. These two functions are also *degenerate* (i.e. have the same energy).

Consider the cases $n_1 = 1, n_2 = 2$ and $n_1 = 2, n_2 = 1$:

$$\psi_{1,2} = (2/L)\sin(\pi x/L)\sin(2\pi y/L), \qquad E_{1,2} = 5(h^2/8mL^2),$$
$$\psi_{2,1} = (2/L)\sin(2\pi x/L)\sin(\pi y/L), \qquad E_{2,1} = 5(h^2/8mL^2).$$

The point to note is that *more than one wavefunction* (two in this case) *correspond to the same energy*. This is the condition of *degeneracy*. In this case, we say that the level with energy $5(h^2/8mL^2)$ is *doubly degenerate*.

The occurrence of degeneracy is related to the symmetry of the system. The two degenerate functions $\psi_{1,2}$ and $\psi_{2,1}$ are shown in Fig. 14.4: because the plane is square, we see that we can convert one into the other simply by rotating the plane by 90°. This is not possible when the plane is not square and then $\psi_{1,2}$ and $\psi_{2,1}$ are non-degenerate. We shall see many examples of degeneracy in the pages that follow (e.g. in the hydrogen atom); and all of them can be traced to the symmetry properties of the system.

14.1 (d) Quantum leaks

If the potential energy of the particle does not rise to infinity when it is i[n] the walls of the container, then the argument that led to eqn (14.1.6) allow[s] the wavefunction to remain non-zero. If the walls are thin (so that th[e] potential energy falls to zero again after a finite distance), the exponenti[al] decay of the wavefunction stops, and it begins to oscillate like th[e] wavefunctions for the inside of the box, Fig. 14.5. This means that th[e] particle might be found on the outside of a container even though accordin[g] to classical mechanics it has insufficient energy to escape. This leakin[g] through classically forbidden zones is called *tunnelling*.

The Schrödinger equation lets us calculate the extent of tunnelling an[d] how it depends on the mass of the particle. In fact, from the result in eq[n] (14.1.6) we can see that, since the wavefunction decreases exponential[ly] inside the wall, and does so with a rate that depends on $\sqrt{m}$, *light particl[es] are more able to tunnel through barriers than heavy ones*. Tunnelling is ve[ry] important for electrons, and moderately important for protons; for heavi[er] particles it is less important. A number of effects in chemistry (e.g. so[me] reaction rates) depend on the ability of the proton to tunnel more readi[ly] than the deuteron.

The kind of problem we can solve with the material developed so far [is] illustrated by the case of a projectile (such as an electron or a proto[n]) incident from the left on a region where its potential energy increas[es] sharply from zero to a finite, constant value V, remains there for a distan[ce] L, and then falls to zero again, Fig. 14.6. This is a model of what happe[ns] when particles are fired at an idealized metal foil or sheet of paper. We c[an] ask for the proportion of incident particles that penetrate the barrier wh[en] their kinetic energy is less than V so that classically none can penetrate.

The strategy of the calculation (and of others like it) is as follows:

(1) Write down the Schrödinger equation for each zone of const[ant] potential.

(2) Write down the general solutions for each zone using eqn (14.1.2) [for] the regions where $V < E$ and eqn (14.1.6) for regions where $V > E$.

(3) Find the coefficients by ensuring that (a) the wavefunction [is] continuous at each zone boundary, and (b) the first derivatives of [the] wavefunctions are also continuous at the zone boundaries.

παράδειγμα -2-

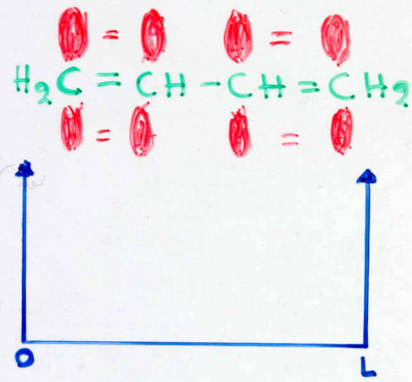
Μοντέλο "Ελεύθερου Ηλεκτρονίου" στο Βουταδιένιο

$C{=}C$: $1.35\,Å$

$C{-}C$: $1.54\,Å$

$m_e = 9.110 \times 10^{-31}\,kg$

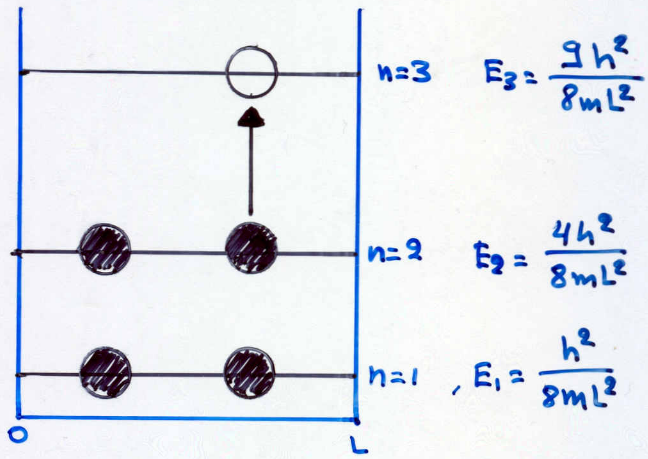
$\left.\right\}\ \Delta E = ?\quad \bar{\nu} = ?$



Λύση για $1e^-$

$L = 2 \times 1.35 + 2 \times 1.54 = 5.78\,Å = 5.78 \times 10^{-10}\,m$

$$E_n = \frac{n^2h^2}{8mL^2}$$



Τοποθέτηση όλων των e^- ανά 2 (απαγορευτική αρχή του Pauli)

$$\Delta E = \frac{h^2}{8mL^2}(3^2 - 2^2) = \frac{5h^2}{8mL^2}\ \ (= E_3 - E_2)$$

$$\Rightarrow \Delta E = \frac{5\,(6.626 \times 10^{-34}\,J.s)}{8\,(9.110 \times 10^{-31}\,Kg)\,(5.78 \times 10^{-10}\,m)^2} \Rightarrow \dots$$

$$\Rightarrow \Delta E = 9.02 \times 10^{-19}\,J \Rightarrow \dots$$

$\Delta E = h\nu$

$\frac{1}{\lambda} = \frac{\nu}{c} \equiv \bar{\nu}$ κυματάριθμος wave number

$\bar{\nu} = 4.54 \times 10^4\,cm^{-1}$

$\bar{\nu}_{exp} = 4.61 \times 10^4\,cm^{-1}$

$$\left.\begin{array}{l}\Delta E = h\nu \\ \nu = \frac{c}{\lambda}\end{array}\right\}\ \Delta E = \frac{hc}{\lambda} \Rightarrow \bar{\nu} = \frac{1}{\lambda} = \frac{\Delta E}{hc} = \frac{(9.02 \times 10^{-19}\,J)}{(6.626 \times 10^{-34}\,Js)(2.99 \times 10^{10}\,cm\,s^{-1})} = 4.54 \times 10^{4}\,cm^{-1}$$

$\Downarrow$

$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$ κυματάριθμος