3.012 Bonding-Structure: Recitation 1 (Solutions)

Erratum

- Usually $\psi(\overrightarrow{r})$ denotes the solution of the S.S.E, and $\Psi(\overrightarrow{r}, t)$ that of the T.D.S.E. Thus, equation (2) should be corrected:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\overrightarrow{r}) + V(\overrightarrow{r})\psi(\overrightarrow{r}) = E\psi(\overrightarrow{r}) \quad (1)$$

  Same correction for (a5):
  $\Psi(x,t) = Ae^{i(kx-\omega t)} + Be^{i(-kx-\omega t)}$ is a solution of the time-dependent Schrödinger equation (T.D.S.E.) on the conditions that $E = \hbar\omega$ and $E = \frac{(\hbar k)^2}{2m}$
  Thank you for pointing that out.

1 Wave-Particle Duality

Recall

- *mass of an hydrogen atom* $=$ *m(H)* $=$ *mass proton* $= 1.67 \times 10^{-27}$ *kg* $\approx$ *1 g/mol*

Solution I

(i) de Broglie relation: $\lambda(photon) \times p(photon) = h$
(ii) momentum-velocity relation: $p(H_2) = m(H_2)v(H_2) = 2m(H)v(H_2)$

Consequently, the momenta $p(H_2)$ and $p(photon)$ are equal provided that:

$$\begin{aligned} 2m(H)v(H_2) &= \frac{h}{\lambda(photon)} \\ v(H_2) &= \frac{h}{2m(H)\lambda(photon)} \\ v(H_2) &= \underline{0.708 \text{ m/s}} \end{aligned}$$

2 Solving the Schrödinger Equation

Recall

- *derivative of an exponential:* $\frac{d}{dx}e^{ax+b} = ae^{ax+b}$.

  Examples:

$$\frac{d}{dx}(5+2i)e^{i3x-2} = (5+2i)(3i)e^{i3x-2} \quad ; \quad \frac{d}{dx}i\sqrt{2}e^{3x-2i} = i3\sqrt{2}e^{3x-2i}$$

$$\frac{d}{dx}e^{ikx} = ike^{ikx} \quad ; \quad \frac{d^2}{dx^2}e^{ikx} = (ik)^2 e^{ikx}$$

$$\frac{\partial}{\partial t}e^{ikx-i\omega t} = -i\omega e^{ikx-i\omega t} \quad ; \quad \frac{\partial}{\partial x}e^{ikx-i\omega t} = ike^{ikx-i\omega t}$$

- *in general, only x, y, z and t can vary. k, ω, a, A, B, etc are constants.*

Remark

It is important that you be able to answer questions (a1) to (c4)

Solution II

- *Free Electron in 1D*: $V(x) = 0$

  (a1) FALSE

  i) S.S.E.: $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x)$

  ii) $\frac{d}{dx}4e^{ikx} = 4ike^{ikx}$; $\frac{d^2}{dx^2}4e^{ikx} = 4(ik)^2e^{ikx}$.

  Hence, $\psi(x) = 4e^{ikx}$ satisfies $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = \frac{\hbar^2k^2}{2m}\psi(x)$, which is the S.S.E. with energy $E = \frac{\hbar^2k^2}{2m}$.

  Similarly (replace k with $5k$), $\psi(x) = 4e^{i5kx}$ satisfies $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = \frac{\hbar^2(5k)^2}{2m}\psi(x)$, which is the stationary Schrödinger equation with energy $E = \frac{25\hbar^2k^2}{2m}$.

  iii) Thus, the two wavefunctions $\psi(x) = 4e^{ikx}$ and $\psi(x) = 4e^{i5kx}$ are solutions of the S.S.E. but with DIFFERENT energies.

  (a2) TRUE

  i) S.S.E.: $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x)$

  ii) $\frac{d}{dx}4\cos(kx) + 2e^{i\frac{\pi}{4}}\sin(kx) = 4(-k)\sin(kx) + 2e^{i\frac{\pi}{4}}k\cos(kx)$

$\frac{d^2}{dx^2}4\cos(kx) + 2e^{i\frac{\pi}{4}}\sin(kx) = 4(-k)k\cos(kx) + 2e^{i\frac{\pi}{4}}k(-k)\sin(kx)$

iii) Hence, $\psi(x)$ satisfies $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = \frac{\hbar^2 k^2}{2m}\psi(x)$.

(a3) <u>FALSE</u>

i) S.S.E.: $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x)$

ii) $\frac{d^2}{dx^2}Ae^{ikx} + Be^{-2ikx} = A(ik)^2e^{ikx} + B(-2ik)^2e^{-2ikx} = -k^2(Ae^{ikx} + 4Be^{-2ikx})$

iii) Hence, $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = \frac{\hbar^2 k^2}{2m}(Ae^{ikx} + \mathbf{4}B^2e^{-2ikx})$ which can not be written as $E(Ae^{ikx} + B^2e^{-2ikx})$ (because of the factor 4 before B). Consequently, $\psi(x)$ does not satisfy the S.S.E.

(a4) <u>TRUE</u>

i) S.S.E.: $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x)$

ii) $\frac{d^2}{dx^2}A\sin(kx) + B\cos(kx) = -k^2(A\sin(kx) + B\cos(kx))$.

ii) Hence, $\psi(x)$ satisfies $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = \frac{\hbar^2 k^2}{2m}\psi(x)$.

(a5) <u>TRUE</u>

i) T.D.S.E.: $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t)$

ii) $\frac{\partial^2}{\partial x^2}Ae^{i(kx-\omega t)} + Be^{i(-kx-\omega t)} = -k^2(Ae^{i(kx-\omega t)} + Be^{i(-kx-\omega t)})$.

iii) $\frac{\partial}{\partial t}Ae^{i(kx-\omega t)} + Be^{i(-kx-\omega t)} = -i\omega(Ae^{i(kx-\omega t)} + Be^{i(-kx-\omega t)})$

iv) Thus $\psi(x)$ satisfies the T.D.S.E. $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t)$ on the condition that:

$$\begin{aligned} -\frac{\hbar^2}{2m}(-k^2) &= i\hbar(-i\omega) \\ \frac{\hbar^2 k^2}{2m} &= \hbar\omega \end{aligned} \tag{2}$$

(note that, similarly to the stationary case, $\frac{\hbar^2 k^2}{2m}$ is equal to E the energy of the particle)

- *Free Electron in 2D*: $V(x,y) = 0$

  (b1) <u>TRUE</u>

  i) S.S.E.: $-\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2}\psi(x,y) + \frac{\partial^2}{\partial y^2}\psi(x,y) = E\psi(x,y)$

ii) $\frac{\partial^2}{\partial x^2}(4+2i)e^{i(2x+3y)} = (4+2i)(2i)^2 e^{i(2x+3y)} = -4\psi(x,y)$

$\frac{\partial^2}{\partial y^2}(4+2i)e^{i(2x+3y)} = (4+2i)(3i)^2 e^{i(2x+3y)} = -9\psi(x,y)$

iii) Thus, $-\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2}\psi(x,y) + \frac{\partial^2}{\partial y^2}\psi(x,y) = (9+4)\frac{\hbar^2}{2m}\psi(x,y)$

iv) $\psi(x,y)$ satisfies the S.S.E. with energy $\frac{13\hbar^2}{2m}\psi(x,y)$

(b2) TRUE

i) S.S.E.: $-\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2}\psi(x,y) + \frac{\partial^2}{\partial y^2}\psi(x,y) = E\psi(x,y)$

ii) $\frac{\partial^2}{\partial x^2}A\cos(k_x x)\sin(k_y y) = -k_x^2\psi(x,y)$

$\frac{\partial^2}{\partial y^2}A\cos(k_y x)\sin(k_y y) = -k_y^2\psi(x,y)$

iii) Thus, $-\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2}\psi(x,y) + \frac{\partial^2}{\partial y^2}\psi(x,y) = \frac{\hbar^2(k_x^2+k_y^2)}{2m}\psi(x,y)$

iv) $\psi(x,y)$ satisfies the S.S.E. with energy $\frac{\hbar^2(k_x^2+k_y^2)}{2m}$

- *Electron in a 1D Infinite Box (Infinite Square Well)*: $V(x) = \begin{cases} +\infty & \text{if } x<0 \\ 0 & \text{if } 0<x<a \\ +\infty & \text{if } a<x \end{cases}$

(c1) FALSE

i) S.S.E. : $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x)$

ii) $V(x)$ is infinite outside the box (that is, when $x<0$ or $x>a$). As a consequence, the electron can not be found in that spatial region: $psi(x)=0$ when $x<0$ or $x>a$ (recall: the probability of finding the electron at a position x_0 is related to the square modulus of $psi(x_0)$; see problem III).

iii) Thus, we only need to solve the S.S.E. in the spatial interval $0<x<a$ with the constraint that $\psi(x)=0$ at the boundaries of the box ($x=0$ and $x=a$). We end up with:

$$\begin{cases} -\frac{\mathbf{\hbar^2}}{\mathbf{2m}}\frac{d^2\psi}{dx^2}(x) = \mathbf{E}\psi(\mathbf{x}) \text{ for } 0<x<a \\ \psi(0)=0 \\ \psi(a)=0 \end{cases} \quad (3)$$

which is different from $\begin{cases} \frac{d^2\psi}{dx^2}(x) = \mathbf{0} \text{ for } 0<x<a \\ \psi(0)=0 \\ \psi(a)=0 \end{cases}$

(c2) FALSE

i) From the preceding the S.S.E. can be rewritten as: $\begin{cases} -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}(x) = E\psi(x) \text{ for } 0 < x < a \\ \psi(0) = 0 \\ \psi(a) = 0 \end{cases}$

ii) $\frac{d^2}{dx^2} i\sqrt{2}\cos(\frac{3\pi x}{a}) = -(\frac{3\pi}{a})^2 i\sqrt{2}\cos(\frac{3\pi x}{a})$

Thus, $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}(x) = \frac{9\hbar^2\pi^2}{2ma^2}\psi(x)$. The first equation is satisfied.

iii) However, $\psi(0) = i\sqrt{2}\cos(0) = i\sqrt{2} \neq 0$ and $\psi(a) = i\sqrt{2}\cos(3\pi x) = -i\sqrt{2} \neq 0$ Thus, the boundary conditions are not satisfied.

(c3) <u>TRUE</u>

i) S.S.E. and boundary conditions: $\begin{cases} -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}(x) = E\psi(x) \text{ for } 0 < x < a \\ \psi(0) = 0 \\ \psi(a) = 0 \end{cases}$

ii) $\frac{d^2}{dx^2} A\sin(\frac{n\pi x}{a}) = -(\frac{n\pi}{a})^2 A\sin(\frac{n\pi x}{a})$

Thus, $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}(x) = \frac{\hbar^2 n^2\pi^2}{2ma^2}\psi(x)$. The first equation is satisfied.

iii) $\psi(0) = A\sin(0) = 0$ and $\psi(a) = A\sin(n\pi x) = 0$. The boundary conditions are satisfied.

iv) Conclusion: $\psi(x)$ is a solution of the S.S.E. with energy $\frac{\hbar^2 n^2\pi^2}{2ma^2}$.

(c4) <u>TRUE</u>

The statement (c4) is equivalent to (c3): the only difference is that the energy $E = (\hbar^2 n^2\pi^2)/(2ma^2)$ has been rewritten as $E = (h^2 n^2)/(8ma^2)$

- *Electron in a 2D Infinite Box*: $V(x,y) = \begin{cases} 0 & \text{if } 0 < x < a \text{ and } 0 < y < b \\ +\infty & \text{elsewhere} \end{cases}$

(d1) <u>FALSE</u>

0) This one is a bit challenging!

i) As previously, the S.S.E. can be rewritten as:

$$\begin{cases} -\frac{\hbar^2}{2m}(\frac{\partial^2\psi}{\partial x^2}(x,y) + (\frac{\partial^2\psi}{\partial y^2}(x,y)) = E\psi(x,y) \text{ for } 0 < x < a \text{ and } 0 < y < b \\ \psi = 0 \text{ at the boundaries of the box} \end{cases}$$

ii) $\frac{\partial^2}{\partial x^2} A\sin(\frac{l\pi x}{a})\sin(\frac{m\pi y}{b}) = A\sin(\frac{m\pi y}{b})\frac{\partial^2}{\partial x^2}\sin(\frac{l\pi x}{a}) = A\sin(\frac{m\pi y}{b})\{-(\frac{l\pi}{a})^2\sin(\frac{l\pi x}{a})\}$

Similarly,

$\frac{\partial^2}{\partial y^2} A\sin(\frac{l\pi x}{a})\sin(\frac{m\pi y}{b}) = A\sin(\frac{l\pi x}{a})\frac{\partial^2}{\partial y^2}\sin(\frac{m\pi y}{b}) = A\sin(\frac{l\pi x}{a})\{-(\frac{m\pi}{b})^2\sin(\frac{m\pi y}{b})\}$

iii) As a consequence, $-\frac{\hbar^2}{2m}(\frac{\partial^2\psi}{\partial x^2}(x,y) + (\frac{\partial^2\psi}{\partial y^2}(x,y) = \frac{\hbar^2\pi^2}{2m}\left(\frac{l^2}{a^2}+\frac{m^2}{b^2}\right)\psi(x,y)$. The first equation is satisfied but with a DIFFERENT energy $E = \frac{\hbar^2\pi^2}{2m}\left(\frac{l^2}{a^2}+\frac{m^2}{b^2}\right) \neq \frac{\hbar^2}{4m}\left(\frac{l^2}{a^2}+\frac{m^2}{b^2}\right)$

(note however that the boundary conditions are satisfied)

- *General Properties of the Schrödinger Equation*

  (e1) FALSE

  0) This one is even more challenging!

  i) $\psi_a(x)$ is a solution of the S.S.E. with energy E_a:

  $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_a(x) + V(x)\psi_a(x) = E_a\psi_a(x)$

  ii) $\psi_b(x)$ is a solution of the S.S.E. with energy E_b:

  $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_b(x) + V(x)\psi_b(x) = E_b\psi_b(x)$

  iii) We want to know whether $A\psi_a(x) + B\psi_b(x)$ is also a solution. To this end we calculate:

  $\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right\}(A\psi_a(x) + B\psi_b(x))$

  $= A\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_a(x) + V(x)\psi_a(x)\right\} + B\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_b(x) + V(x)\psi_b(x)\right\}$

  $= AE_a\psi_a(x) + BE_b\psi_b(x)$

  iv) Since E_a is different from E_b, $AE_a\psi_a(x) + BE_b\psi_b(x)$ can not be rewritten as $E(A\psi_a(x) + B\psi_b(x))$. Hence, $A\psi_a(x) + B\psi_b(x)$ is not a solution.

  ($A\psi_a(x) + B\psi_b(x)$ is a solution of the S.S.E only if $E = E_a = Eb$)

  (e2) TRUE

  0) You may need to study 13.4 to answer this one.

  i) T.D.S.E. :

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\overrightarrow{r},t) + V(\overrightarrow{r})\Psi(\overrightarrow{r},t) = i\hbar\frac{\partial\Psi}{\partial t}(\overrightarrow{r},t) \quad (4)$$

  (note, as usual, that V is assumed to be time-independent)

  ii) S.S.E. :

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\overrightarrow{r}) + V(\overrightarrow{r})\psi(\overrightarrow{r}) = E\psi(\overrightarrow{r}) \quad (5)$$

  iii) We want to know whether $\Psi(\overrightarrow{r},t) = \psi(\overrightarrow{r}) \times e^{-i\frac{Et}{\hbar}}$ is a solution of the T.D.S.E.

To this end, we calculate $-\frac{\hbar^2}{2m}\nabla^2\Psi(\overrightarrow{r},t)+V(\overrightarrow{r})\Psi(\overrightarrow{r},t)$ and $i\hbar\frac{\partial\Psi}{\partial t}(\overrightarrow{r},t)$:

$$\begin{aligned}
-\frac{\hbar^2}{2m}\nabla^2\Psi(\overrightarrow{r},t)+V(\overrightarrow{r},t)\Psi(\overrightarrow{r},t) &= \left\{-\frac{\hbar^2}{2m}\nabla^2+V(\overrightarrow{r})\right\}\psi(\overrightarrow{r})\times e^{-i\frac{Et}{\hbar}} \\
&= e^{-i\frac{Et}{\hbar}}\left\{-\frac{\hbar^2}{2m}\nabla^2+V(\overrightarrow{r})\right\}\psi(\overrightarrow{r}) \\
&= E\psi(\overrightarrow{r})e^{-i\frac{Et}{\hbar}} \text{ (from ii)} \qquad (6)
\end{aligned}$$

$$\begin{aligned}
i\hbar\frac{\partial\Psi}{\partial t}(\overrightarrow{r},t) &= i\hbar\frac{\partial}{\partial t}(\overrightarrow{r},t)\psi(\overrightarrow{r})\times e^{-i\frac{Et}{\hbar}} \\
&= \psi(\overrightarrow{r})i\hbar\frac{\partial}{\partial t}e^{-i\frac{Et}{\hbar}} \\
&= \psi(\overrightarrow{r})i\hbar(-i\frac{E}{\hbar})e^{-i\frac{Et}{\hbar}} \\
&= E\psi(\overrightarrow{r})e^{-i\frac{Et}{\hbar}} \qquad (7)
\end{aligned}$$

iv) Thus $-\frac{\hbar^2}{2m}\nabla^2\Psi(\overrightarrow{r},t)+V(\overrightarrow{r})\Psi(\overrightarrow{r},t)$ and $i\hbar\frac{\partial\Psi}{\partial t}(\overrightarrow{r},t)$ are equal. The T.S.D.E. equation is satisfied.

3 Electron Density, Probability, Normalization

Solution III

(a) The electron is necessarily somewhere in the one-dimensional space. In other words, the probability of finding the electron in the spatial region $-\infty < x < +\infty$ is 1=100%. Thus, the wavefunction must satisfy the normality condition: $\int_{+\infty}^{-\infty}\psi^*(x)\psi(x)dx = 1$.

(b) To normalize $\psi_1(x)$, we calculate $\int_{+\infty}^{-\infty}\psi_1^*(x)\psi_1(x)dx$.
i) Since $\psi_1(x)$ equal to zero outside the box, we have $\int_{+\infty}^{-\infty}\psi_1^*(x)\psi_1(x)dx = \int_0^a\psi_1^*(x)\psi_1(x)dx$.
ii) Moreover, $\psi_1(x)$ is a real function. Thus, $\int_0^a\psi_1^*(x)\psi_1(x)dx = \int_0^a\psi_1^2(x)dx$
iii) Using the integral relation $\int_0^a\sin^2(\frac{n\pi x}{a})dx = \frac{a}{2}$, we obtain
$\int_0^a\psi_1^2(x)dx = \int_0^a A_1^2\sin^2(\frac{\pi x}{a})dx = A_1^2\frac{a}{2}$
iv) Consequently, $\psi_1(x)$ is normalized provided that $\frac{aA_1^2}{2}=1$, that is $A_1=\sqrt{\frac{2}{a}}$.
Finally, $\psi_1(x)=\sqrt{\frac{2}{a}}\sin(\frac{\pi x}{a})$
Similarly, $\psi_6(x)=\sqrt{\frac{2}{a}}\sin(\frac{6\pi x}{a})$

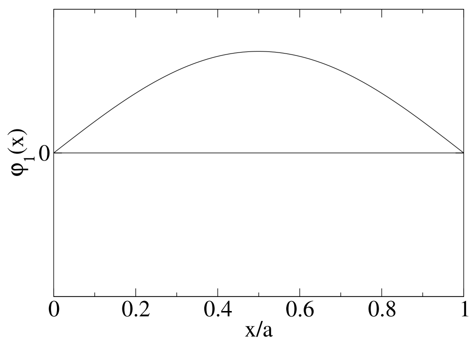
(c) $\psi_1(x)$, $\psi_6(x)$, $\psi_1^*(x)\psi_1(x) = \psi_1^2(x)$ and $\psi_6^*(x)\psi_6(x) = \psi_6^2(x)$ are plotted on the next page.

To estimate the probability of finding an electron of wavefunction $\psi_1(x)$ in the spatial interval $0 < x < a/2$, we can calculate $\int_0^{a/2} \psi_1^*(x)\psi_1(x)dx$ analytically. It is however simpler to determine $\int_0^{a/2} \psi_1^*(x)\psi_1(x)dx$ graphically.

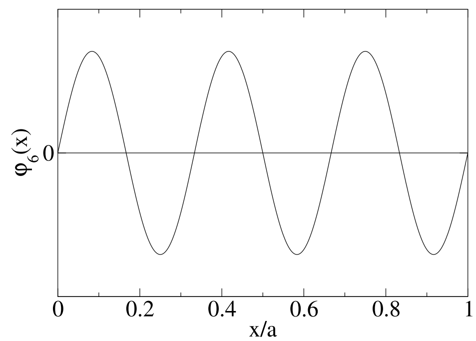
$\psi_1^*(x)\psi_1(x) = \psi_1^2(x)$ is symmetric with respect to $x = a/2$. Moreover, the total integral (area between the curve and the horizontal axis) is equal to 1. As a consequence, $\int_0^{a/2} \psi_1^*(x)\psi_1(x)dx = 1/2$.

The probability of finding an electron of wavefunction $\psi_1(x)$ in the spatial interval $0 < x < a/2$ is 1/2=50%.

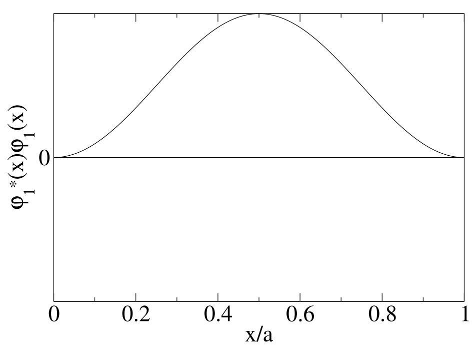
With a similar reasoning, from the graph of $\psi_6^*(x)\psi_6(x)$, the probability of finding an electron of wavefunction $\psi_6(x)$ in the spatial interval $a/3 < x < 2a/3$ is 1/3=33.33%.


φ1(x)
0
0
0.2
0.4
0.6
0.8
1
x/a

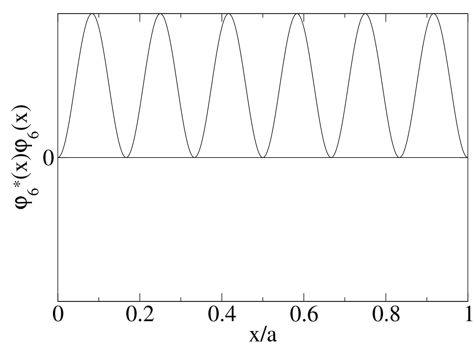
(a)


φ6(x)
0
0
0.2
0.4
0.6
0.8
1
x/a

(b)


φ1*(x)φ1(x)
0
0
0.2
0.4
0.6
0.8
1
x/a

(c)


φ6*(x)φ6(x)
0
0
0.2
0.4
0.6
0.8
1
x/a

(d)

4 Spectrum

Problem IV

The first eigenfunctions (wavefunctions satisfying the S.S.E.) for a particle in a box are shown together with the corresponding eigenvalues (energies of the electron wavefunctions). The energy scale is shown on the left in units of $h^2/(8ma^2)$. The graphs of wavefunction are the oscillating curves. The zero of each wavefunction graph is indicated by the dashed line.

(cf. Engel, Reid page 323)