PAPER CODE NO.
MATH325

THE UNIVERSITY
of LIVERPOOL

JANUARY 2003 ANSWERS

QUANTUM MECHANICS

TIME ALLOWED : Two Hours and a Half

These are brief answers, just to allow you to check your own results. You should show much more working, and write more explanation, than you see here!

1 (i) *Determine which, if any, of the following operators could represent an observable in quantum mechanics*

$$\hat{A} = x\frac{d}{dx}, \quad \hat{B} = i(x\frac{d}{dx} + \frac{1}{2})$$

stating clearly any assumptions you make.

(ii) *A particle at some moment in time is described by the wave function*

$$\psi(x) = \begin{cases} c(a^2 - x^2) & : \quad |x| \le a \\ 0 & : \quad otherwise, \end{cases}$$

where c and a are real positive constants. Find the normalisation constant c in terms of a.

Find the expectation values $\langle \hat{x} \rangle$ *and* $\langle \hat{x}^2 \rangle$ *with respect to the given wave function.*

Deduce that the uncertainty Δx *in a measurement of the position of the particle is given by* $\Delta x = \frac{a}{\sqrt{7}}$.

(i) Integrating by parts

$$\langle \hat{A}\psi|\phi\rangle = -\langle \psi|\phi\rangle - \langle \psi|\hat{A}\phi\rangle \neq \langle \psi|\hat{A}\phi\rangle$$

so $\hat{A}$ is *not* Hermitian, so it could *not* represent an observable.

For the other operator, integrating by parts gives

$$\langle \hat{B}\psi|\phi\rangle = \langle \psi|\hat{B}\phi\rangle$$

so $\hat{B}$ *is* Hermitian, and it can represent an observable.

(ii) For correct normalisation

$$\int_{-a}^{a} c^2(a^2 - x^2)^2 \, dx = 1 \qquad \Rightarrow \qquad c = \sqrt{\frac{15}{16a^5}}.$$

The expectation values needed are

$$\begin{aligned} \langle x \rangle &= c^2 \int_{-a}^{a} x(a^2 - x^2)^2 \, dx = 0 \quad \text{(odd integrand)} \\ \langle x^2 \rangle &= c^2 \int_{-a}^{a} x^2(a^2 - x^2)^2 \, dx = \cdots = \frac{a^2}{7} \\ \Rightarrow \Delta x &= \frac{a}{\sqrt{7}} \end{aligned}$$

2(i) *A particle of mass m is confined to the region $0 \leq x \leq L$ of the x-axis. Write down the corresponding time-independent Schrödinger equation for the problem and hence find the normalised eigenfunctions of the Hamiltonian.*

Show that the energy eigenvalues are

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2} \qquad (n = 1, 2, 3 \ldots)$$

At a particular moment, the particle is in a state described by the normalised wave function

$$\psi(x) = \begin{cases} -Ax & : \quad 0 \leq x \leq \frac{L}{2} \\ A(x-L) & : \quad \frac{L}{2} < x \leq L \\ 0 & : \quad x < 0 \quad or \quad x > L \end{cases}$$

where A is a real, positive normalisation constant.

(ii) Determine the normalisation constant A.

(iii) Calculate the probability, expressed as a percentage, that a measurement of the energy will give the result E_1.

The Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\phi(x)}{dx^2} = E\phi(x) \qquad \text{with} \quad \phi(0) = \phi(L) = 0.$$

The solutions (standard bookwork) are

$$\begin{aligned} \phi_n(x) &= \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \qquad 0 \leq x \leq L, \\ E_n &= \frac{\hbar^2 \pi^2 n^2}{2mL^2} \qquad (n = 1, 2, 3 \ldots). \end{aligned}$$

(i) To normalise

$$\int_0^L |\psi(x)|^2 \, dx = 1 \qquad \Rightarrow \qquad A = \sqrt{\frac{12}{L^3}}$$

(ii) The overlap integral is

$$\begin{aligned} c_1 &= \int_0^L \phi_1^*(x)\psi(x) \, dx = -A\sqrt{\frac{2}{L}} \int_0^{L/2} x \sin \frac{\pi x}{L} \, dx + A\sqrt{\frac{2}{L}} \int_{L/2}^{L} (x-L) \sin \frac{\pi x}{L} \, dx \\ &= \cdots = -\frac{4\sqrt{6}}{\pi^2} \end{aligned}$$

The probability of getting result E_1 is

$$P(E_1) = |c_1|^2 = \frac{96}{\pi^4} = 98.6\% \, .$$

3. *A beam of identical particles of mass m and energy $E > 0$ is travelling along the x-axis from $x < 0$ and is incident on a potential step*

$$\begin{aligned} V(x) &= V_0 \qquad x \geq 0 \\ V(x) &= 0 \qquad x < 0 \end{aligned}$$

where V_0 is a constant. Suppose that $0 < E < V_0$.

(i) Write down an expression for the current density j_I for a beam of particles with wave-function $\psi(x) = Ae^{ikx}$. For the potential step above, evaluate the reflection coefficient R, defined as the ratio of the reflected current density to the incident current density.

(ii) Deduce the transmission coefficient T, and comment on the result.

(iii) Calculate the relative probability of finding a particle at position x (> 0) compared with that of finding one at the origin ($x = 0$). Comment on the physical significance of this result.

(iv) Consider, instead, the case $E > V_0$. Describe, without further calculation, in what respect you would expect the nature of the solution to differ from that which you have already provided.

(i) The current density is $j_I = \frac{\hbar k}{m}|A|^2$.

To solve the Schrödinger equation we make

$$\begin{aligned} \psi_I(x) &= Ae^{ikx} + Be^{-ikx} \qquad x \leq 0 \\ \psi_{II}(x) &= Ce^{-Kx} \qquad x > 0 \\ \text{with} \quad & \frac{\hbar^2 k^2}{2m} = E, \qquad \frac{\hbar^2 K^2}{2m} = V_0 - E. \end{aligned}$$

Matching ψ and $\frac{d\psi}{dx}$ at $x = 0$ gives

$$A = C\frac{k + iK}{2k}, \quad B = C\frac{k - iK}{2k}.$$

$$\text{so} \quad R = \frac{j_R}{j_I} = \left|\frac{B}{A}\right|^2 = 1$$

(ii) $R + T = 1$ so $T = 0$. Even though ψ penetrates into the classically forbidden region $x > 0$, the flux there is zero.

(iii) The relative probability is

$$\frac{|\psi_{II}(x)|^2}{|\psi_{II}(0)|^2} = e^{-2Kx}.$$

There is barrier penetration, but it drops exponentially with distance into the forbidden region.

(iv) If $E > V_0$ we find oscillating wave solutions in both regions. Now we can have some transmission, expect $0 \leq T \leq 1$.

4. *The Hamiltonian for a particle of mass m moving on the x-axis in a harmonic oscillator potential can be written in the form $H = (a^\dagger a + \frac{1}{2})\hbar\omega$ where the frequency ω is a positive constant, and where $[a, a^\dagger] = 1$. The position x and momentum p are given by*

$$x = \frac{i}{\sqrt{2}\alpha}(a - a^\dagger) \quad \textit{and} \quad p = \frac{\hbar\alpha}{\sqrt{2}}(a + a^\dagger), \qquad \textit{where} \quad \alpha = \sqrt{\frac{m\omega}{\hbar}}$$

.

(i) *Show by induction that $[a, (a^\dagger)^n] = n(a^\dagger)^{n-1}$, for n a positive integer.*
(ii) *The normalised eigenfunctions of the Hamiltonian are given by*

$$\psi_n = \frac{1}{\sqrt{n!}}(a^\dagger)^n \psi_0, \quad n \geq 0,$$

where $a\psi_0 = 0$. Show that $a\psi_n = \sqrt{n}\psi_{n-1}$ and *$a^\dagger\psi_n = \sqrt{n+1}\psi_{n+1}$.*
(iii) *By writing $x\psi_n$, $p\psi_n$ in terms of ψ_{n-1}, ψ_{n+1}, compute the uncertainties Δx and Δp for the state ψ_n.*
(iv) *Find $\Delta x \Delta p$ for the state ψ_n and comment on the result. [You may find the following identity useful:*
$[A, BC] = B[A, C] + [A, B]C$ for operators A, B and C.]

(i) Prove $\quad [a, (a^\dagger)^n] = n(a^\dagger)^{n-1} \qquad (*)$
The hypothesis (*) is true for $n = 1$, ($[a, a^\dagger] = 1$). Using the identity in the hint,

$$[a, (a^\dagger)^k a^\dagger] = (a^\dagger)^k [a, a^\dagger] + [a, (a^\dagger)^k] a^\dagger$$

Now suppose that (*) holds for $n = k$, the above becomes

$$[a, (a^\dagger)^{k+1}] = (a^\dagger)^k + k(a^\dagger)^k = (k+1)(a^\dagger)^k,$$

i.e. (*) also holds for $k+1$. The hypothesis (*) holds for $n = 1$, if it holds for any n it also holds for $n+1$, so by induction it holds for all positive integers.

$$\text{(ii)} \quad a\psi_n = \frac{1}{\sqrt{n!}} a(a^\dagger)^n \psi_0 = \frac{1}{\sqrt{n!}} \left\{ (a^\dagger)^n a + n(a^\dagger)^{n-1} \right\} \psi_0 = \sqrt{n}\, \psi_{n-1}.$$

$$a^\dagger \psi_n = \frac{1}{\sqrt{n!}}(a^\dagger)^{n+1}\psi_0 = \sqrt{n+1}\, \psi_{n+1}$$

$$\text{(iii)} \quad x\psi_n = \frac{i}{\alpha\sqrt{2}}(\sqrt{n}\, \psi_{n-1} - \sqrt{n+1}\, \psi_{n+1})$$

$$p\psi_n = \frac{\hbar\alpha}{\sqrt{2}}(\sqrt{n}\, \psi_{n-1} + \sqrt{n+1}\, \psi_{n+1})$$

$$\Rightarrow \quad \langle \psi_n | x\psi_n \rangle = 0; \qquad \langle \psi_n | p\psi_n \rangle = 0;$$

$$\langle x\psi_n | x\psi_n \rangle = \frac{1}{2\alpha^2}(n + (n+1));$$

$$\langle p\psi_n | p\psi_n \rangle = \frac{\hbar^2\alpha^2}{2}(n + (n+1)).$$

$$\Rightarrow \quad \Delta x = \frac{1}{\alpha}\sqrt{n + \tfrac{1}{2}}; \qquad \Delta p = \hbar\alpha\sqrt{n + \tfrac{1}{2}}$$

(iv) $\Delta x \Delta p = (n + \frac{1}{2})\hbar$. This is $\geq \frac{1}{2}\hbar$, as required by Heisenberg's uncertainty principle. When $n = 0$ the uncertainty is exactly the minimumum value allowed.

5. *Given that the angular momentum operators* L_i $(i = 1, 2, 3)$ *satisfy the commutation relations* $[L_1, L_2] = i\hbar L_3$ *(and cyclic permutations), show that*

$$[\mathbf{L}^2, L_1] = [\mathbf{L}^2, L_2] = [\mathbf{L}^2, L_3] = 0$$

where $\mathbf{L}^2 = L_1^2 + L_2^2 + L_3^2$.

*From the above commutation relations it is possible to deduce the following results (*which you may assume*). There exist normalised eigenstates* $|l, m\rangle$ *such that*

$$L_3|l, m\rangle = \hbar m|l, m\rangle, \qquad \mathbf{L}^2|l, m\rangle = \hbar^2 l(l + 1)|l, m\rangle,$$

where $2l$ *is a positive integer and the possible values of* m *are* $-l, -l+1, \ldots l-1, l$. *Moreover,*

$$L_+|l, m\rangle = M_{l,m}|l, m + 1\rangle \quad \text{and} \quad L_-|l, m\rangle = N_{l,m}|l, m - 1\rangle,$$

where $L_+ = L_1 + iL_2$ *and* $L_- = L_1 - iL_2$, *and* $M_{l,m}$ *and* $N_{l,m}$ *are real, positive constants.*

(i) *Show that*

$$L_-L_+ = \mathbf{L}^2 - L_3^2 - \hbar L_3$$

and, by considering the norm of $L_+|l, m\rangle$, *show that*

$$M_{l,m} = \hbar\sqrt{l(l + 1) - m(m + 1)}\,.$$

(ii) *A particle is in a state such that* $l = 1$. *Write down the allowed values of* m *(corresponding to the eigenvalues of* L_3*) and evaluate the matrix elements*

$$\langle 1, 0|L_+|1, 0\rangle \qquad \text{and} \qquad \langle 1, 1|L_+|1, 0\rangle\,.$$

(iii) *Find all other non-zero elements of the matrix*

$$\langle 1, m'|L_+|1, m\rangle\,.$$

and display your results for the full 3×3 *matrix where the rows are labelled by values of* m' *and the columns by values of* m.

(iv) *Obtain a similar matrix representation for* L_-, *and hence find a matrix representation for* L_1.

[*You may assume that in (iv),* $N_{l,m}$ *is given by*

$$N_{l,m} = \hbar\sqrt{l(l + 1) - m(m - 1)}\,.]$$

(i) $L_-L_+ = (L_1 - iL_2)(L_1 + iL_2) = L_1^2 + i[L_1, L_2] + L_2^2 = \mathbf{L}^2 - L_3^2 - \hbar L_3$. The mod-squared of $L_+|l,m\rangle$ is

$$\begin{aligned} \langle l,m|L_+^\dagger L_+|l,m\rangle = \langle l,m|L_-L_+|l,m\rangle &= \langle l,m|\left(\mathbf{L}^2 - L_3^2 - \hbar L_3\right)|l,m\rangle \\ &= \hbar^2\left\{l(l+1) - m(m+1)\right\} \\ \Rightarrow M_{l,m} = \hbar\sqrt{l(l+1) - m(m+1)} & \end{aligned}$$

(ii) The allowed values of m run from $-l$ to $+l$ in steps of 1, so $m \in \{-1, 0, 1\}$.

$$\begin{aligned} \langle 1,0|L_+|1,0\rangle &= M_{1,0}\langle 1,0|1,1\rangle = 0. \qquad \text{(orthogonality)} \\ \langle 1,1|L_+|1,0\rangle &= M_{1,0}\langle 1,1|1,1\rangle = \hbar\sqrt{2} \end{aligned}$$

(iii) The scalar product is 0 unless $m' = m + 1$. The only other non-zero element is

$$\langle 1,0|L_+|1,-1\rangle = M_{1,-1}\langle 1,0|1,0\rangle = \hbar\sqrt{2}.$$

The matrix form of L_+ for $l = 1$ is

$$L_+ = \hbar\sqrt{2}\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} \qquad \begin{matrix} m' = 1 \\ m' = 0 \\ m' = -1 \end{matrix}$$

$$m = \quad 1 \quad 0 \quad -1$$

(iv) Similarly L_- in matrix form gives

$$L_- = \hbar\sqrt{2}\begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

(Either use $L_- = L_+^\dagger$, or the $N_{l,m}$ values from the hint.)
From the definitions, $L_1 = \frac{1}{2}(L_+ + L_-)$, so

$$L_1 = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

(note that L_1 is Hermitian, as it should be).

6(i) *Using integration by parts, or otherwise, show that for* $n \geq 2$

$$I_n = \frac{n-1}{2\beta^2} I_{n-2}\,, \qquad \textit{where} \quad I_n \equiv \int_0^\infty r^n e^{-\beta^2 r^2}\, dr\,.$$

Given that $I_0 = \frac{\sqrt{\pi}}{2\beta}$, *find* I_2. *Evaluate* I_1 *and deduce the value of* I_5.

(ii) The Hamiltonian for a particle of mass m *moving in three dimensions under the influence of a three-dimensional harmonic oscillator potential is*

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \frac{1}{2}m\omega^2 r^2\,,$$

where $r = |\mathbf{r}| = \sqrt{x^2+y^2+z^2}$ *and the radial part of the Laplacian operator is*

$$\nabla^2_{\rm rad} = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}.$$

Given that the normalised ground state wave function is

$$\psi_0(\mathbf{r}) = A e^{-\frac{1}{2}\beta^2 r^2}\,,$$

where A *is real, determine* β *and the ground state energy* E_0. *Calculate also the normalisation constant* A.

(iii) The potential is perturbed by the addition of a term λr^5 *where* λ *is small. Use first order perturbation theory to obtain an approximation to the perturbed ground state energy in the form* $E_0 + \lambda K$ *where* K *is a constant which you should find.*

[*Standard results from perturbation theory may be assumed without proof.*]

(i) Proof:

$$I_{n-2} = \int_0^\infty r^{n-2} e^{-\beta^2 r^2}\, dr = \left[\frac{r^{n-1}}{n-1} e^{-\beta^2 r^2}\right]_0^\infty - \int_0^\infty \frac{r^{n-1}}{n-1} (-2\beta^2 r) e^{-\beta^2 r^2}\, dr = \frac{2\beta^2}{n-1} I_n$$

To find I_1, make the substitution $r^2 = u$

$$I_1 = \int_0^\infty r e^{-\beta^2 r^2}\, dr = \frac{1}{2}\int_0^\infty e^{-\beta^2 u}\, du = -\frac{1}{2\beta^2}\left[e^{-\beta^2 u}\right]_0^\infty = \frac{1}{2\beta^2}$$

From I_0 and I_1 we can deduce

$$I_2 = \frac{1}{2\beta^2} I_0 = \frac{\sqrt{\pi}}{4\beta^3}, \qquad I_5 = \frac{4}{2\beta^2} I_3 = \frac{4}{2\beta^2}\frac{2}{2\beta^2} I_1 = \frac{1}{\beta^6}$$

(ii) Plug ψ_0 into the Schrödinger equation $\hat{H}\psi_0 = E_0\psi_0$. Since ψ_0 is independent of θ, ϕ only ∇^2_{rad} is needed.

$$\begin{aligned} \hat{H}\psi_0(\mathbf{r}) &= -\frac{\hbar^2}{2m}(\psi_0'' + \frac{2}{r}\psi_0') + \frac{1}{2}m\omega^2 r^2 \psi_0 \\ &= \left(-\frac{\hbar^2}{2m}(\beta^4 r^2 - 3\beta^2) + \frac{1}{2}m\omega^2 r^2\right) A e^{-\frac{1}{2}\beta^2 r^2} \end{aligned}$$

ψ_0 is a solution of the Schrödinger equation if the r^2 terms cancel, i.e. if

$$\beta^2 = \frac{m\omega}{\hbar}$$

In that case ψ_0 is an eigenfunction of $\hat{H}$ with eigenvalue

$$E_0 = \frac{\hbar^2}{2m} 3\beta^2 = \frac{3}{2}\hbar\omega.$$

For correct normalisation

$$\int_0^\infty 4\pi r^2\, |\psi_0(\mathbf{r})|^2\, dr = 1 \qquad \Rightarrow \qquad A = \left(\frac{m\omega}{\hbar\pi}\right)^{3/4}$$

(iii) Perturbation theory says that to first order the energy change is

$$\Delta E_0 = \langle \psi_0 | \lambda r^5 \psi_0 \rangle = \int_0^\infty 4\pi r^2\, \lambda r^5\, |\psi_0(\mathbf{r})|^2\, dr = 4\pi A^2 I_7 \lambda$$

Finding I_7 from part (i) we get

$$E = \frac{3}{2}\hbar\omega + K\lambda \qquad \text{with} \quad K = \frac{12}{\beta^5\sqrt{\pi}} = \frac{12}{\sqrt{\pi}}\left(\frac{\hbar}{m\omega}\right)^{5/2}.$$

7.(i) *Give a statement of the variational principle and explain briefly how it may be used to obtain an upper bound on the ground state energy E_0 of a system with Hamiltonian $\hat{H}$.*

(ii) *The motion of a particle of mass m in one dimension is described by the Hamiltonian*

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \lambda|x| \qquad (\lambda > 0)\,.$$

Consider, in turn, each of the following two normalised wave functions

$$\psi_1(x) = A_1 e^{-\alpha|x|} \qquad \textit{and} \qquad \psi_2(x) = A_2(1+\alpha|x|)e^{-\alpha|x|}\,,$$

Here, $\alpha > 0$ and

$$A_1 = \sqrt{\alpha}\,, \qquad A_2 = \sqrt{\frac{2\alpha}{5}}\,.$$

By applying the variational method, decide which (if any) of these is a suitable trial wave function for the given problem. Where appropriate, give a variational upper bound for the ground state energy.

Note: in (ii) you may use without proof the result

$$I_n(b) \equiv \int_0^\infty x^n e^{-bx}\,dx = \frac{n!}{b^{n+1}}$$

when $b > 0$.

(i) The variational principle proves that for any normalised state ψ

$$\langle\psi|\hat{H}\psi\rangle \geq E_0.$$

Choose a trial wave function ψ with some free parameters, and minimise $\langle\psi|\hat{H}\psi\rangle$ w.r.t. the parameters. This minimum value of $\langle\hat{H}\rangle$ is an upper bound on the ground state energy, which is usually close to the true E_0.

(ii) (a) For the first wave function we get

$$\begin{aligned}
\langle T\rangle &= \frac{1}{2m}\int_{-\infty}^{\infty}[\hat{p}\psi_1]^*[\hat{p}\psi_1]\,dx = \cdots = \frac{\hbar^2\alpha^2}{2m}\\
\langle V\rangle &= \lambda\int_{-\infty}^{\infty}|\psi_1|^2|x|\,dx = \cdots = \frac{\lambda}{2\alpha}\\
\Rightarrow \langle\hat{H}\rangle &= \frac{\hbar^2\alpha^2}{2m} + \frac{\lambda}{2\alpha}
\end{aligned}$$

The minimum value is

$$\langle\hat{H}\rangle = \frac{3}{2}\frac{\hbar^2}{m}\left(\frac{m\lambda}{2\hbar^2}\right)^{\frac{2}{3}} = 0.945\left(\frac{\hbar^2\lambda^2}{m}\right)^{\frac{1}{3}} \quad \text{when} \quad \alpha = \left(\frac{m\lambda}{2\hbar^2}\right)^{\frac{1}{3}}.$$

(b) Similarly the second wave function gives

$$\langle\hat{H}\rangle = \frac{\hbar^2\alpha^2}{10m} + \frac{9\lambda}{10\alpha}$$

which has a minimum value of

$$\langle \hat{H} \rangle = \frac{3}{10}\frac{\hbar^2}{m}\left(\frac{9m\lambda}{2\hbar^2}\right)^{\frac{2}{3}} = 0.818\left(\frac{\hbar^2\lambda^2}{m}\right)^{\frac{1}{3}} \quad \text{when} \quad \alpha = \left(\frac{9m\lambda}{2\hbar^2}\right)^{\frac{1}{3}}.$$

Both functions are suitable. The second gives a lower answer, so it must be a better estimate.

Notes:

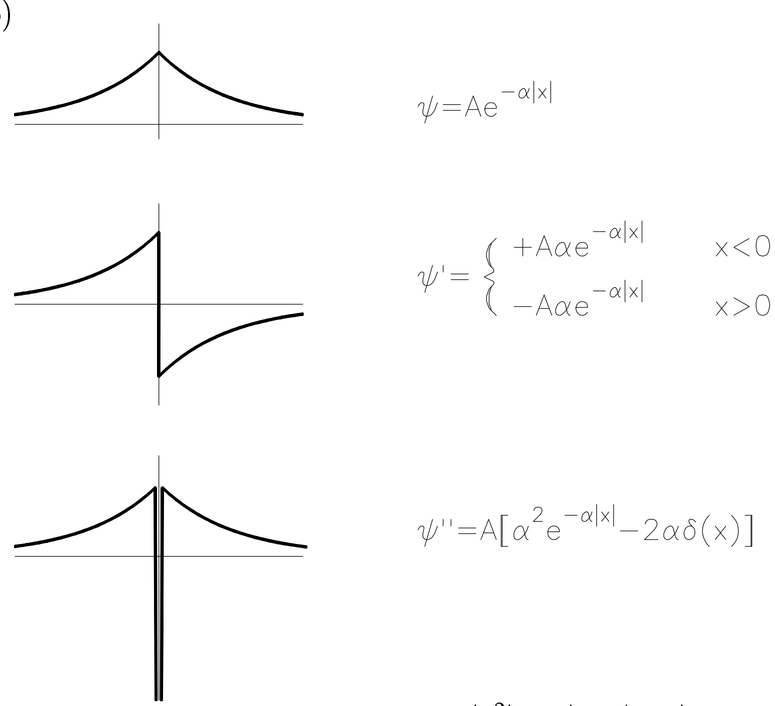
First a physics note, then a warning about a mistake that's easy to make.

(a) The equation can be solved with the help of a special function, the Airy function. The true ground state energy is

$$E_0 = 0.8086\left(\frac{\hbar^2\lambda^2}{m}\right)^{\frac{1}{3}},$$

so the bound from ψ_2 is just 1% over.

(b)



Calculating the kinetic energy from $\langle p^2 \rangle = \langle \hat{p}\psi_1 | \hat{p}\psi_1 \rangle$ is straight-forward, but if you calculate it from $\langle p^2 \rangle = \langle \psi_1 | \hat{p}^2 \psi_1 \rangle$, (which should always give the same answer) it is easy to make a mistake. The first derivative of ψ_1 makes a jump at $x = 0$, so the second derivative has a δ-function at $x = 0$. It's easy to forget the δ-function and get a silly answer (that $\langle p^2 \rangle$ is negative). The easiest way of avoiding this problem is to always calculate $\langle p^2 \rangle$ by the first method ($\langle \hat{p}\psi_1 | \hat{p}\psi_1 \rangle$), which avoids taking second derivatives. If you do want to calculate it from the second derivative, remember that wave-functions with sudden changes in slope will give you δ functions in ψ''.