Chem221a : Solution Set 5

David W.H. Swenson

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Problem 1

No matter what representation we use, Hamiltonians of the sort we almost always use in quantum mechanics can be written as $\hat{H} = \frac{\hat{p}^2}{2m} + V(x)$. The tricky part is that we need to represent the operators $\hat{p}$ and $\hat{x}$ is our choice of representation. For convenience, we almost always choose a representation where one of those operators is just a number — mostly the position representation, where the position operator $\hat{x} = x$, where x is a real number.

Some problems, this one being an example, lend themselves to solutions in the momentum representation.[1] Knowing that this will eventually lead to a differential equation (because the operator $\hat{x}$ in the p representation is a differential operator), we'll isolate $\hat{x}\,|\psi\rangle$ on one side:

$$E\,|\psi\rangle = \hat{H}\,|\psi\rangle \tag{1}$$

$$= \left(\frac{\hat{p}^2}{2m} + V(\hat{x})\right)|\psi\rangle \tag{2}$$

$$= \left(\frac{\hat{p}^2}{2m} + E - F(\hat{x} - a)\right)|\psi\rangle \tag{3}$$

$$0 = \left(\frac{\hat{p}^2}{2m} - F\hat{x} + Fa\right)|\psi\rangle \tag{4}$$

$$\hat{x}\,|\psi\rangle = \left(\frac{\hat{p}^2}{2mF} + a\right)|\psi\rangle \tag{5}$$

Now we'll multiply on left by $\langle p'|$ for both sides of this equation:

$$\langle p'|\hat{x}|\psi\rangle = \left\langle p'\middle|\frac{\hat{p}^2}{2mF} + a\middle|\psi\right\rangle \tag{6}$$

$$-\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}p'}\langle p'|\psi\rangle = \left(\frac{{p'}^2}{2mF} + a\right)\langle p'|\psi\rangle \tag{7}$$

$$\frac{\mathrm{d}}{\mathrm{d}p'}\psi(p') = -\frac{i}{\hbar}\left(\frac{{p'}^2}{2mF} + a\right)\psi(p') \tag{8}$$

[1] How can you guess whether you should solve a problem in the position or momentum representation? The question is which differential equation will be easier to solve. If you use the position representation, you always have a second-order differential equation with some arbitrarily complicated ***

In general, the solution to the differential equation $\frac{\mathrm{d}}{\mathrm{d}x} f(x) = g(x) f(x)$ is $f(x) = \exp(\int \mathrm{d}x\, g(x))$. So the result for our situation is:

$$\psi(p') = \exp\left(\int \mathrm{d}p' \; -\frac{i}{\hbar}\left(\frac{p'^2}{2mF} + a\right)\right) \tag{9}$$

$$= \exp\left(-\frac{i}{\hbar}\left(\frac{p'^3}{2mF} + p'a + c\right)\right) \tag{10}$$

$$= C' \exp\left(-\frac{i}{\hbar}\left(\frac{p'^3}{2mF} + p'a\right)\right) \tag{11}$$

We're almost there — now we just have to do the inverse Fourier transform to get the position representation of this wavefunction (actually, we don't have to *do* it, we just need to write it down:

$$\psi(x') = \frac{1}{\sqrt{2\pi\hbar}} \int_{\mathbb{R}} \mathrm{d}p' \, e^{ix'p'/\hbar} \psi(p') \tag{12}$$

$$= C \int_{\mathbb{R}} \mathrm{d}p' \, \exp\left(-\frac{i}{\hbar}\left(\frac{p'^3}{2mF} + p'a\right) + \frac{i}{\hbar} x'p'\right) \tag{13}$$

$$= C \int_{\mathbb{R}} \mathrm{d}p' \, \exp\left(-\frac{i}{\hbar}\left(\frac{p'^3}{2mF} - p'(x' - a)\right)\right) \quad \square \tag{14}$$

Problem 2

In solving this problem, I'm going to introduce a few tricks to make the solution a little faster. In particular, let's notice that the matrix B is block diagonal in the matrix in question, and the lower block (the 2x2 non-diagonal matrix) corresponds to the $\{|-a\rangle\}$ eigenspace of the matrix A. That means that any ket which is a linear combination of kets in that subspace, in particular the eigenkets of B in that subspace, will be an eigenket of A with eigenvalue $-a$.

(a) Obviously one of the eigenvalues of B is b, with associated eigenvector $\left(\begin{smallmatrix}1\\0\\0\end{smallmatrix}\right)$. So let's find the eigenvalues associated with the remaining 2x2 subspace:

$$0 = \det\left(\lambda \hat{1} - \begin{pmatrix} 0 & -ib \\ ib & 0 \end{pmatrix}\right) \tag{15}$$

$$= \det\begin{pmatrix} \lambda & ib \\ -ib & \lambda \end{pmatrix} \tag{16}$$

$$= \lambda^2 - b^2 \tag{17}$$

$$\lambda = \pm b \tag{18}$$

This means that for the entire matrix B, we have one eigenvector with eigenvalue $-b$, and two eigenvectors with eigenvalue $+b$. Therefore the B does have a degenerate eigenvalue spectrum.

(b) Although we really should calculate the commutator as it acts on an arbitrary ket, we'll do that implicitly rather than explicitly (that is to say that it's pretty clear that you can stick an arbitrary ket on the right and that it won't change anything).

$$[A,B] = \begin{pmatrix} a & 0 & 0 \\ 0 & -a & 0 \\ 0 & 0 & -a \end{pmatrix} \begin{pmatrix} b & 0 & 0 \\ 0 & 0 & -ib \\ 0 & ib & 0 \end{pmatrix} - \begin{pmatrix} b & 0 & 0 \\ 0 & 0 & -ib \\ 0 & ib & 0 \end{pmatrix} \begin{pmatrix} a & 0 & 0 \\ 0 & -a & 0 \\ 0 & 0 & -a \end{pmatrix} \tag{19}$$

$$= \begin{pmatrix} ab & 0 & 0 \\ 0 & 0 & iab \\ 0 & -iab & 0 \end{pmatrix} - \begin{pmatrix} ab & 0 & 0 \\ 0 & 0 & iab \\ 0 & -iab & 0 \end{pmatrix} \tag{20}$$

$$= 0 \tag{21}$$

Note that part (c) has already told us that this will be the answer: we can't have simultaneous eigenkets unless these operators commute!

(c) For this part, we'll again take advantage of the fact that we only need to look at the 2x2 subspace associated with the $-a$ eigenvalue of operator A. Any vector from that subspace will have eigenvalue $-a$, so once we find a vector which is an eigenvector of B, we have a vector which is a simultaneous eigenvector of A and B.

We'll start by finding the eigenket from this subspace associated with the eigenvalue $+b$:

$$bc_1 + ibc_2 = 0 \implies ic_1 = c_2 \tag{22}$$

Normalizing, we obtain the vector

$$|-a, +b\rangle = \begin{pmatrix} 1/\sqrt{2} \\ i/\sqrt{2} \end{pmatrix} \tag{23}$$

For the eigenvalue $-b$ we find

$$-bc_1 + ibc_2 = 0 \implies c_2 = -ic_1 \tag{24}$$

When normalized, this gives us the vector

$$|-a, -b\rangle = \begin{pmatrix} 1/\sqrt{2} \\ -i/\sqrt{2} \end{pmatrix} \tag{25}$$

Putting all of this together for the three-dimensional space, we have the set of eigenvectors:

$$\left\{ |+a, +b\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, |-a, +b\rangle = \begin{pmatrix} 0 \\ 1/\sqrt{2} \\ i/\sqrt{2} \end{pmatrix}, |-a, -b\rangle = \begin{pmatrix} 0 \\ 1/\sqrt{2} \\ -i\sqrt{2} \end{pmatrix} \right\} \tag{26}$$

As we can see, no two eigenkets have the same set of eigenvalues. Therefore, we each ket is completely characterized by the eigenvalues of A and B.

As a brief aside, it's interesting to note that it is impossible to simultaneously measure the B as $-b$ and A and $+a$. The two are mutually exclusive.

Problem 3

(a) For both of these, all we have to do is show the two sides to be equal. Particularly in the first one, I'll work by adjusting both sides until they agree. First, we'll remember that $\langle [A,B] \rangle = \langle [\Delta A, \Delta B] \rangle$:

$$(\langle \psi | \Delta A)(\Delta A |\psi\rangle) \langle \psi | (\Delta B)^2 | \psi \rangle = \frac{1}{4} |\langle \psi | [\Delta A, \Delta B] | \psi \rangle|^2 \tag{27}$$

$$= \frac{1}{4} |\langle \psi | (\Delta A)(\Delta B) | \psi \rangle - \langle \psi | (\Delta B)(\Delta A) | \psi \rangle|^2 \tag{28}$$

Now we use the fact that $\Delta A |\psi\rangle = \lambda \Delta B |\psi\rangle$, along with its dual, $\langle \psi | \Delta A = \lambda^* \langle \psi | \Delta B$.

$$\langle \psi | (\lambda^* \Delta B)(\lambda \Delta B) | \psi \rangle \langle \psi | (\Delta B)^2 | \psi \rangle = \frac{1}{4} \left| \langle \psi | \lambda^* (\Delta B)^2 | \psi \rangle - \langle \psi | \lambda (\Delta B)^2 | \psi \rangle \right|^2 \tag{29}$$

$$\lambda^* \lambda \langle \psi | (\Delta B)^2 | \psi \rangle^2 = \frac{1}{4} \left| (\lambda^* - \lambda) \langle \psi | (\Delta B)^2 | \psi \rangle \right|^2 \tag{30}$$

By definition, $|\lambda|^2 = \lambda^* \lambda$ and $|\langle \psi | M | \psi \rangle|^2 = \langle \psi | M | \psi \rangle^2$ for any Hermitian M. Also, since λ is pure imaginary, $\lambda^* - \lambda = -2\lambda$. Putting all of these facts into the above expression, we find:

$$|\lambda|^2 \left| \langle \psi | (\Delta B)^2 | \psi \rangle \right|^2 = \frac{1}{4} \left| 2\lambda \langle \psi | (\Delta B)^2 | \psi \rangle \right|^2 \tag{31}$$

$$= |\lambda|^2 \left| \langle \psi | (\Delta B)^2 | \psi \rangle \right|^2 \tag{32}$$

Yay! It's true!

Now for the "moreover" bit: we'll do something similar, but just simplify one side. As we showed on the right hand side of the previous part, $\langle [A,B] \rangle = -2\lambda \langle (\Delta B)^2 \rangle$, so quite simply that gives us:

$$-\frac{\langle [A,B] \rangle}{2 \langle (\Delta B)^2 \rangle} = -\frac{-2\lambda \langle (\Delta B)^2 \rangle}{2 \langle (\Delta B)^2 \rangle} \tag{33}$$

$$= \lambda \quad \square \tag{34}$$

(b) Let's start by plugging in the definition of λ and of ΔA, and using the canonical commutator relation $[x,p] = i\hbar$:

$$\Delta p |\psi\rangle = \lambda (\Delta x) |\psi\rangle \tag{35}$$

$$(\hat{p} - \langle p \rangle) |\psi\rangle = \frac{- \langle [p,x] \rangle}{2 \langle (\Delta x)^2 \rangle} (\hat{x} - \langle x \rangle) |\psi\rangle \tag{36}$$

$$\hat{p} |\psi\rangle = \left(\frac{-(-i\hbar)}{2 \langle (\Delta x)^2 \rangle} (\hat{x} - \langle x \rangle) + \langle p \rangle \right) |\psi\rangle \tag{37}$$

Now let's take the position representation of all of that (namely, let's multiply on the right by a position eigenbra):

$$\langle x'|\hat{p}|\psi\rangle = \left\langle x' \middle| \frac{i\hbar}{2\left\langle(\Delta x)^2\right\rangle}\left(\hat{x} - \langle x\rangle\right) + \langle p\rangle \middle| \psi \right\rangle \tag{38}$$

$$\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x'}\langle x'|\psi\rangle = \left(\frac{i\hbar}{2\left\langle(\Delta x)^2\right\rangle}\left(x' - \langle x\rangle\right) + \langle p\rangle\right)\langle x'|\psi\rangle \tag{39}$$

$$\frac{\mathrm{d}}{\mathrm{d}x'}\psi(x') = \left(-\frac{x' - \langle x\rangle}{2\left\langle(\Delta x)^2\right\rangle} + \frac{i}{\hbar}\langle p\rangle\right)\psi(x') \tag{40}$$

Just as we did in problem 1, we're going to solve this first order differential equation in the usual way:

$$\begin{aligned}
\psi(x') &= \exp\left(\int \mathrm{d}x' \, \frac{-1}{2\left\langle(\Delta x)^2\right\rangle}\left(x' - \langle x\rangle\right) + \frac{i}{\hbar}\langle p\rangle\right) && (41)\\
&= \exp\left(\frac{-1}{2\left\langle(\Delta x)^2\right\rangle}\left(\frac{1}{2}x'^2 - \langle x\rangle x'\right) + \frac{i}{\hbar}\langle p\rangle x' + k\right) && (42)\\
&= \exp\left(\frac{-1}{4\left\langle(\Delta x)^2\right\rangle}\left(x'^2 - 2\langle x\rangle x' + \langle x\rangle^2\right) + \frac{i}{\hbar}\langle p\rangle x' + \frac{\langle x\rangle^2}{4\left\langle(\Delta x)^2\right\rangle} + k\right) && (43)\\
&= \exp\left(-\frac{\left(x' - \langle x\rangle\right)^2}{4\left\langle(\Delta x)^2\right\rangle} + \frac{i}{\hbar}\langle p\rangle x' + k'\right) && (44)
\end{aligned}$$

Here we have absorbed the constant $\langle x\rangle^2/(4\left\langle(\Delta x)^2\right\rangle)$ into the constant k. We'll deal with all of that in a moment when we normalize the wavefunction anyway. In fact, let's define the normalization constant $C = e^{k'}$:

$$\psi(x') = C\exp\left(-\frac{\left(x' - \langle x\rangle\right)^2}{4\left\langle(\Delta x)^2\right\rangle} + \frac{i}{\hbar}\langle p\rangle x'\right) \tag{45}$$

Normalization requires

$$\begin{aligned}
1 &= \int_{\mathbb{R}} \mathrm{d}x' \, \psi^*(x')\psi(x') && (46)\\
&= \int_{\mathbb{R}} \mathrm{d}x' \left(C^*\exp\left(-\frac{\left(x' - \langle x\rangle\right)^2}{4\left\langle(\Delta x)^2\right\rangle} - \frac{i}{\hbar}\langle p\rangle x'\right)\right)\left(C\exp\left(-\frac{\left(x' - \langle x\rangle\right)^2}{4\left\langle(\Delta x)^2\right\rangle} + \frac{i}{\hbar}\langle p\rangle x'\right)\right) && (47)\\
&= |C|^2\int_{\mathbb{R}} \mathrm{d}x' \, \exp\left(-\frac{\left(x' - \langle x\rangle\right)^2}{2\left\langle(\Delta x)^2\right\rangle}\right) && (48)\\
&= |C|^2\sqrt{\pi(2\left\langle(\Delta x)^2\right\rangle)} && (49)
\end{aligned}$$

So choosing C to be real and positive (by phase convention) we obtain the result:

$$\psi(x') = \left(\frac{1}{2\pi\left\langle(\Delta x)^2\right\rangle}\right)^{1/4}\exp\left(-\frac{\left(x' - \langle x\rangle\right)^2}{4\left\langle(\Delta x)^2\right\rangle} + \frac{i}{\hbar}\langle p\rangle x'\right) \tag{50}$$

This is (to within a typo on the problem set) what we were to show.

Problem 4

This problem is an example of first order perturbation theory on a Hamiltonian derived from the Hückel approximation. These words don't really matter right now, but keep this problem in mind when we get to perturbation theory.

(a) As always, the first thing we must do is to determine a matrix representation of the Hamiltonian. The set of $\{|\phi_i\rangle\}$ will be convenient.

Since these are the eigenkets of the unperturbed H_0, the matrix representation of H_0 is pretty easy:

$$H_0 = \begin{pmatrix} E_0 & 0 & 0 \\ 0 & E_0 & 0 \\ 0 & 0 & E_0 \end{pmatrix} \tag{51}$$

Now we work on the perturbation Hamiltonian, W. You may be able to immediately identify the resulting matrix, but I'll show some detail on how to get it.

Let's start with the first line: $W|\phi_A\rangle = -a|\phi_B\rangle$. Clearly, the only bra which will give a nonzero result is $\langle\phi_B|$. So this will make the first column of the matrix representation of W into:

$$\begin{pmatrix} 0 \\ -a \\ 0 \end{pmatrix} \tag{52}$$

The exact same will be true for the third line, with $|\phi_C\rangle$, which will give us the third column of the matrix. With a similar analysis, the second line gives us the second column of the matrix, and putting the three columns in order, find the matrix representation of W:

$$\begin{pmatrix} 0 & -a & 0 \\ -a & 0 & -a \\ 0 & -a & 0 \end{pmatrix} \tag{53}$$

Now we have the unperturbed Hamiltonian and the perturbation, both expressed as matrices. The total Hamiltonian is

$$H = H_0 + W \tag{54}$$

$$= \begin{pmatrix} E_0 & 0 & 0 \\ 0 & E_0 & 0 \\ 0 & 0 & E_0 \end{pmatrix} + \begin{pmatrix} 0 & -a & 0 \\ -a & 0 & -a \\ 0 & -a & 0 \end{pmatrix} \tag{55}$$

$$= \begin{pmatrix} E_0 & -a & 0 \\ -a & E_0 & -a \\ 0 & -a & E_0 \end{pmatrix} \tag{56}$$

The energies will be the eigenvalues of this matrix, so let's find them:

$$
\begin{aligned}
0 &= \det \begin{pmatrix} E - E_0 & a & 0 \\ a & E - E_0 & a \\ 0 & a & E - E_0 \end{pmatrix} && (57) \\
&= (E - E_0)^3 - 2a^2(E - E_0) && (58) \\
&= (E - E_0)((E - E_0)^2 - 2a^2) && (59) \\
&= (E - E_0)(E - (E_0 - a\sqrt{2}))((E - (E_0 + a\sqrt{2})) && (60)
\end{aligned}
$$

Therefore, we have three possible values for the energy: $E = \{E_0, E_0 + a\sqrt{2}, E_0 - a\sqrt{2}\}$. With those energy eigenvalues, let's calculate the energy eigenkets.

$\left|E = E_0 - a\sqrt{2}\right\rangle$: We'll use the first and third lines of the matrix. For an eigenvector of components x_1, x_2, x_3, we get the equations:

$$
\begin{aligned}
0 &= -\sqrt{2}x_1 + x_2 && (61) \\
0 &= -\sqrt{2}x_3 + x_2 && (62)
\end{aligned}
$$

Putting these together, we see that

$$x_1 = x_3 = x_2/\sqrt{2} \qquad (63)$$

As a normalized vector, this becomes:

$$|E_-\rangle = \left|E_0 - a\sqrt{2}\right\rangle = \begin{pmatrix} 1/2 \\ 1/\sqrt{2} \\ 1/2 \end{pmatrix} \qquad (64)$$

$|E = E_0\rangle$: Lines 1 and 3 from the matrix are the same, and tell us that $x_2 = 0$. Line 2 tells us that $x_1 = -x_3$. As a normalized vector, this becomes:

$$|E_0\rangle = \begin{pmatrix} 1/\sqrt{2} \\ 0 \\ -1/\sqrt{2} \end{pmatrix} \qquad (65)$$

$\left|E = E_0 + a\sqrt{2}\right\rangle$: The results here are very similar to the results from the $|E_-\rangle$ state, except the combined equations give $x_1 = x_3 = -x_2/\sqrt{2}$. So the normalized eigenvector is:

$$|E_+\rangle = \left|E_0 + a\sqrt{2}\right\rangle = \begin{pmatrix} 1/2 \\ -1/\sqrt{2} \\ 1/2 \end{pmatrix} \qquad (66)$$

(b) Now we want to calculate the time-dependent probability of getting each of the possible values of D, given that we are starting in the state $|\phi_A\rangle$. Written mathematically, this is:

$$\text{Prob}(D = \delta) = |\langle\delta|\phi_A(t)\rangle|^2 \qquad (67)$$

Let's start off by recognizing that the eigenkets of D are the kets $|\phi_i\rangle$. Specifically, we have $|D=-d\rangle = |\phi_A\rangle$, $|D=0\rangle = |\phi_B\rangle$, and $|D=+d\rangle = |\phi_C\rangle$. So let's plug that in, and then use the definition of the time evolution operator for time-independent Hamiltonians, and finally a resolution of the identity, to get an expression:

$$\begin{aligned}
\mathrm{Prob}(D=\delta) &= \left|\langle\phi_\delta|e^{-iHt\hbar}|\phi_A\rangle\right|^2 && (68)\\
&= \left|\left\langle\phi_\delta\middle|e^{-iHt/\hbar}\sum_i\middle|E_i\right\rangle\left\langle E_i\middle|\phi_A\right\rangle\right|^2 && (69)\\
&= \left|\sum_i\left\langle\phi_\delta\middle|e^{-iE_it/\hbar}\middle|E_i\right\rangle\langle E_i|\phi_A\rangle\right|^2 && (70)\\
&= \left|\sum_i e^{-iE_it/\hbar}\langle\phi_\delta|E_i\rangle\langle E_i|\phi_A\rangle\right|^2 && (71)
\end{aligned}$$

Now we'll use that expression to calculate each of the probabilities.

$$\begin{aligned}
\mathrm{Prob}(D=-d) &= \left|\sum_i e^{-iE_it/\hbar}\langle\phi_A|E_i\rangle\langle E_i|\phi_A\rangle\right|^2 && (72)\\
&= \left|e^{-i(E_0-a\sqrt{2})t/\hbar}\frac{1}{2}\frac{1}{2} + e^{-iE_0t/\hbar}\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}} + e^{-i(E_0+a\sqrt{2})t/\hbar}\frac{1}{2}\frac{1}{2}\right|^2 && (73)\\
&= \left|\frac{1}{2}e^{-iE_0t/\hbar}\left(\frac{1}{2}\left(e^{ia\sqrt{2}t/\hbar}+e^{-ia\sqrt{2}t/\hbar}\right)+1\right)\right|^2 && (74)\\
&= \frac{1}{4}\left|\cos(a\sqrt{2}t/\hbar)+1\right|^2 && (75)\\
\mathrm{Prob}(D=0) &= \left|\sum_i e^{-iE_it/\hbar}\langle\phi_B|E_i\rangle\langle E_i|\phi_A\rangle\right|^2 && (76)\\
&= \left|e^{-i(E_0-a\sqrt{2})t/\hbar}\frac{1}{\sqrt{2}}\frac{1}{2} + e^{-iE_0t/\hbar}0\frac{1}{\sqrt{2}} + e^{-i(E_0+a\sqrt{2})t/\hbar}\frac{-1}{\sqrt{2}}\frac{1}{2}\right|^2 && (77)\\
&= \left|\frac{1}{\sqrt{2}}e^{-iE_0t/\hbar}\left(\frac{1}{2}\left(e^{ia\sqrt{2}t/\hbar}-e^{-ia\sqrt{2}t/\hbar}\right)\right)\right|^2 && (78)\\
&= \frac{1}{2}\sin^2\left(\frac{a\sqrt{2}}{\hbar}t\right) && (79)
\end{aligned}$$

$$\begin{aligned}
\text{Prob}(D = +d) &= \left| \sum_i e^{-iE_i t/\hbar} \langle \phi_C | E_i \rangle \langle E_i | \phi_A \rangle \right|^2 && (80) \\
&= \left| e^{-i(E_0 - a\sqrt{2})t/\hbar} \frac{1}{2}\frac{1}{2} + e^{-iE_0 t/\hbar} \frac{-1}{\sqrt{2}}\frac{1}{\sqrt{2}} + e^{-i(E_0 + a\sqrt{2})t/\hbar} \frac{1}{2}\frac{1}{2} \right|^2 && (81) \\
&= \left| \frac{1}{2} e^{-iE_0 t/\hbar} \left(\frac{1}{2} \left(e^{ia\sqrt{2}t/\hbar} + e^{-ia\sqrt{2}t/\hbar} \right) - 1 \right) \right|^2 && (82) \\
&= \frac{1}{4} \left| \cos(a\sqrt{2}t/\hbar) - 1 \right|^2 && (83) \\
& && (84)
\end{aligned}$$

With very little work, we can show that the sum of these probabilities is 1.