November 24, 2008

PAULI MATRICES

The spin $-\frac{1}{2}$ operator S may be written,

$$\hat{S} = \frac{1}{2}\hbar\hat{\sigma} = \frac{1}{2}\hbar[\hat{\sigma}_x i + \hat{\sigma}_y j + \hat{\sigma}_z k] \tag{4.52}$$

Since

$$[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z$$

hence

$$[\hat{\sigma}_x, \hat{\sigma}_y] = 2i\hat{\sigma}_z(+\text{ cyclic permutations}) \tag{4.53}$$

Other relations for $\hat{S}_i$ hold, but with $\frac{\hbar}{2}$ scaling.

We can construct a matrix-representation for the operators $\hat{\sigma}$, $\hat{S}$ with the $|\alpha\rangle$,$|\beta\rangle$ basis:

eg

$$(\hat{S}_x)_{11} = \langle\alpha|\hat{S}_x|\alpha\rangle = \left\langle \alpha|\frac{|\hat{S}_+ + \hat{S}_-|}{2}\alpha \right\rangle = 0$$

$$(S_x)_{12} = \langle\alpha\hat{S}_x\beta\rangle = \frac{\hbar}{2} \tag{4.54}$$

Hence,

$$\hat{S}_x = \begin{pmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{pmatrix}$$

Similarly,

$$\hat{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \text{and} \quad \hat{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The PAULI MATRICES (drop $\frac{\hbar}{2}$) are:

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}; \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{4.55}$$

PROPERTIES OF PAULI MATRICES σ_i $(i = x, y, z)$

$$\sigma_i^2 = I \tag{4.56a}$$

$$T_r \sigma_i = 0 \tag{4.56b}$$

$$\det\ \sigma_i = -1 \tag{4.56c}$$

$$T_r(\sigma_i \sigma_j) = 2\delta ij \tag{4.56d}$$

Together with the identity matrix, I, the σ_i form a complete set for any 2×2 matrix, M, which may be expanded as a linear combination:

$$M = \sum_{i=x,y,z,0} a_i \sigma_i \tag{4.57a}$$

where

$$a_i = \frac{1}{2} T_r(M\sigma_i) \tag{4.57b}$$

Since, from 4.57a

$$M\sigma_j = \sum_i a_i \sigma_i \sigma_j$$

$$\begin{aligned} \Rightarrow T_r(M\sigma_j) &= \sum_i a_i T_r(\sigma_i \sigma_j) \\ &= 2a_i \delta_{ij} \end{aligned} \tag{4.57b}$$

We can represent the spin-states (spinors) by column vectors:

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Hence an arbitrary spin state $|\chi\rangle$, in this notation is:

$$|\chi\rangle = a \begin{pmatrix} 1 \\ 0 \end{pmatrix} + b \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix} \tag{4.58}$$

We can obtain eigenvectors of an arbitrary spin operator by diagonalising the appropriate matrix.

eg we want e'vectors of $\hat{S}_x$, where:

$$\hat{S}_x|\chi\pm\rangle = \pm\frac{\hbar}{2}|\chi\pm\rangle \tag{4.59}$$

$$\begin{aligned}
\Rightarrow \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} &= \lambda' \begin{pmatrix} a \\ b \end{pmatrix} = \lambda\frac{\hbar}{2}\begin{pmatrix} a \\ b \end{pmatrix} \\
(\lambda' &= \lambda\frac{\hbar}{2} \text{ for convenience})
\end{aligned}$$

$$\Rightarrow \frac{\hbar}{2}\begin{pmatrix} -\lambda & 1 \\ 1 & -\lambda \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = 0, \Rightarrow \begin{vmatrix} -\lambda & 1 \\ 1 & -\lambda \end{vmatrix} = 0$$

$$\lambda^2 - 1 = 0, \quad \Rightarrow \lambda = \pm 1$$

For $\lambda = +1$,

$$\begin{aligned}
S_x|\chi+\rangle &= \lambda'|\chi+\rangle = \frac{\hbar}{2}|\chi+\rangle \\
\frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} &= \frac{\hbar}{2}\begin{pmatrix} a \\ b \end{pmatrix} \Rightarrow \begin{pmatrix} b \\ a \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix} \\
&\Rightarrow a = b
\end{aligned}$$

Normalisation $\Rightarrow |a|^2 + |b|^2 = 1$

So,

$$\begin{aligned}
|\chi+\rangle &= \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \\
&= \frac{1}{\sqrt{2}}(|\alpha\rangle + |\beta\rangle)
\end{aligned}$$

E'value	$+\frac{\hbar}{2}$	$-\frac{\hbar}{2}$
operator		
$\hat{S}_x$	$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$	$\frac{1}{\sqrt{2}}\begin{pmatrix}-1\\1\end{pmatrix}$
$\hat{S}_y$	$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\i\end{pmatrix}$	$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-i\end{pmatrix}$
$\hat{S}_z$	$\begin{pmatrix}1\\0\end{pmatrix}$	$\begin{pmatrix}0\\1\end{pmatrix}$

(4.60)

in previous notation

So, eigenstates of $\hat{S}_x$ are superpositions of the eigenstates of $\hat{S}_z$ (the $|\alpha\rangle, |\beta\rangle$).

We can diagonalise all the matrices to get all e'vectors:

We can calculate eigenvectors of spin operator along arbitrary $\hat{n}$ (unit vector in direction defined by polar angles θ, ϕ)

$$\hat{n} = \sin\theta\cos\phi\hat{i} + \sin\theta\sin\phi\hat{j} + \cos\theta\hat{k}$$

$$\hat{S}_n = \hat{n}\cdot s = \hat{n}\cdot(\hat{S}_x i + \hat{S}_y j + \hat{S}_z k)$$

$$= \sin\theta\cos\phi\hat{S}_x + \sin\theta\sin\phi\hat{S}_y + \cos\theta\hat{S}_z$$

$$\Rightarrow \hat{S}_n = \frac{\hbar}{2}\begin{bmatrix}\cos\theta & \sin\theta e^{-i\phi}\\ \sin\theta e^{i\phi} & -\cos\theta\end{bmatrix} \tag{4.61}$$

We can diagonalise to obtain eig'vectors

$$|n+\rangle = \begin{bmatrix}\cos\left(\frac{\theta}{2}\right)e^{-i\frac{\phi}{2}}\\ \sin\left(\frac{\theta}{2}\right)e^{i\frac{\phi}{2}}\end{bmatrix} \tag{4.61b}$$

$*$ Obtain $|n-\rangle$ as an exercise, ie show that:

$$|n-\rangle = \begin{bmatrix}-\sin\left(\frac{\theta}{2}\right)e^{-i\frac{\phi}{2}}\\ \cos\left(\frac{\theta}{2}\right)e^{i\frac{\phi}{2}}\end{bmatrix} \tag{4.62b}$$

you may find an extra overall phase ie $|n-\rangle = |n-\rangle e^{-i\phi}$ but this is not important.

Rotations

A very useful operator is

$$R_{\hat{n}} = e^{-i\frac{\theta}{2}\hat{n}\cdot\hat{\sigma}} \tag{4.63b}$$

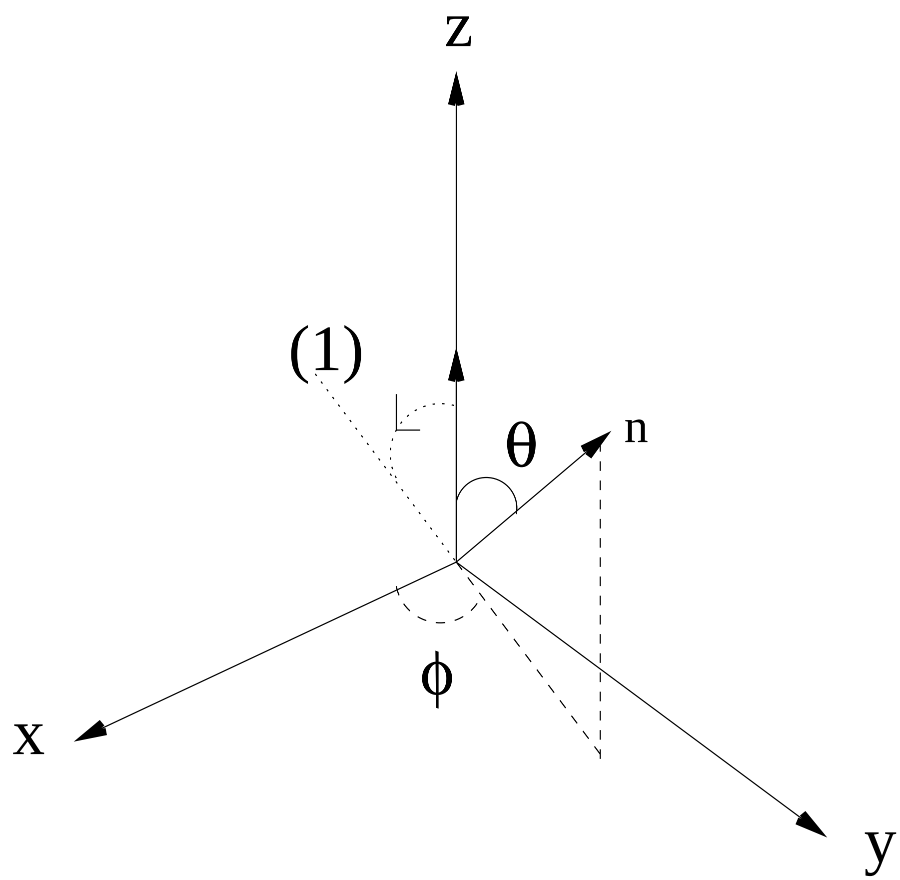
It rotates a spinor by an angle θ about axis $\hat{\mathbf{n}}$. We can obtain $|n+\rangle$ from $|\alpha\rangle$ by a set of rotations.

In general, the angular momentum operators are generators of rotations: you may have covered this in another course. If not, see handout given in class.

ie if $|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ represents a spin pointing along the z axis, to obtain a spin along the $\hat{n} = (\theta, \phi)$ axis we

1. rotate $|\alpha\rangle$ by an angle θ about the $y - axis$ by applying the operator $e^{-i\frac{\theta}{2}\hat{\sigma}_y}$
2. then rotate the resulting vector and angle ϕ about the $z - axis$.

   The figure indicates step (1) - to rotate $|\alpha\rangle$ in the x-z plane about y.



ie

$$|n+\rangle = e^{-i\frac{\phi}{2}\hat{\sigma}_z} e^{-i\frac{\theta}{2}\hat{\sigma}_y} |\alpha\rangle \tag{4.64b}$$

From I.3d we know:

$$e^{-i\frac{\phi}{2}\hat{\sigma}_z} = \cos\frac{\phi}{2}\ I - i\sin\frac{\phi}{2}\sigma_z$$
$$= \begin{bmatrix} e^{-i\phi/2} & 0 \\ 0 & e^{i\phi/2} \end{bmatrix} \tag{4.65b}$$

in matrix form and of course

$$e^{-i\frac{\theta}{2}\hat{\sigma}_y} = \cos\frac{\theta}{2}\ I - i\sin\frac{\theta}{2}\sigma_y = \begin{bmatrix} \cos\theta/2 & -\sin\theta/2 \\ \sin\theta/2 & \cos\theta/2 \end{bmatrix} \tag{4.66b}$$

hence

$$|n+\rangle = \begin{bmatrix} e^{-i\phi/2} & 0 \\ 0 & e^{i\phi/2} \end{bmatrix} \begin{bmatrix} \cos\theta/2 & -\sin\theta/2 \\ \sin\theta/2 & \cos\theta/2 \end{bmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{4.67b}$$

By matrix multiplication, verify that the state in Eq.4.61b is recovered.

Expectation values

We can also obtain expectation values from spinors, eg:

$$\begin{aligned} \langle\chi\sigma_z\chi\rangle &= (a^*b^*)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} \\ &= (a^*b^*)\begin{pmatrix} a \\ -b \end{pmatrix} = |a|^2 - |b|^2 \end{aligned} \tag{4.68a}$$

(compare with (4.37)!)

We can also obtain *SCALAR PRODUCTS* take another state $|\eta\rangle = c|\alpha\rangle + d|\beta\rangle$

$$\langle\eta|\chi\rangle = (c^*d^*)\begin{pmatrix} a \\ b \end{pmatrix} = c^*a + d^*b \tag{4.69b}$$

SPATIAL DEPENDENCE

In general, the quantum state of a spin $-\frac{1}{2}$ p'cle also has a spatial dependence:

$$\Psi(r,s,t) = \sum_{m_s=-s}^{+s} c_{ms}\psi_{ms}(r,t)|sm_s\rangle$$

for spin $-\frac{1}{2}$,

$$\Psi(r,s,t) \equiv \begin{pmatrix} C_{\frac{1}{2}} & \psi_{\frac{1}{2}}(r,t) \\ C_{-\frac{1}{2}} & \psi_{-}\frac{1}{2}(r,t) \end{pmatrix}$$

$$\begin{aligned} \langle\hat{S}_z\rangle &= \langle\Psi\hat{S}_z\Psi\rangle \\ &= \frac{\hbar}{2}[|C_{\frac{1}{2}}|^2 - |C_{-\frac{1}{2}}|^2] \end{aligned} \tag{4.70}$$

SPINS IN MAGNETIC FIELDS

This section enables us, in a simple way to combine the techniques of Section 1 (Time evolution operators) Section 2 (Time-dependent perturbation theory) and even (in one example) Section 3 (WKB theory) with Section 4. It also enables us to look at key ideas underpinning the physics of NMR (nuclear magnetic resonace) and MRI (magnetic resonance imaging).

A spin-1/2 particle in a magnetic field **B** experiences a Hamiltonian:

$$\hat{H} = -\mu \cdot \mathbf{B} = -\mu \mathbf{S} \cdot \mathbf{B} \tag{4.71}$$

μ depends on whether we consider electron spin or nuclear spin since $\mu_e \gg \mu_N$. For example, MRI usually involves nuclear spins of H-atoms. hence

$$\hat{H} = -\mu \sigma \cdot \mathbf{B} \tag{4.72}$$

In a time independent field, the time-evolution operator becomes:

$$\hat{U}(t) = \exp -\frac{i\hat{H}t}{\hbar} = e^{i\mu \frac{t}{2} \sigma \cdot \mathbf{B}} \tag{4.73}$$

Note that in this section we use $\hat{U}(t)$ to denote $\hat{T}(t,0)$ the time evolution operator of Section 1.

Let $\mathbf{B} = B_0 \hat{z}$ ie the external field defines our z-axis. We can express the operator $\hat{U}$ in matrix form (see Sec I.6) using $|\alpha\rangle, |\beta\rangle$ as a basis. Then

$$\hat{U}(t) = \begin{bmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{bmatrix} \tag{4.74}$$

where $U_{12} = \langle \alpha | \hat{U} | \beta \rangle$ etc etc.

So $U_{11} =< \alpha | \exp \frac{i\mu t}{2} \sigma_z | \alpha >$. Let $\omega_0 = -\mu B_0$.

Then, $U_{11} = \exp \frac{-i\omega_0 t}{2}$ and

$$\hat{U}(t) = \begin{pmatrix} e^{-i \frac{\omega_0}{2} t} & 0 \\ 0 & e^{i \frac{\omega_0}{2} t} \end{pmatrix} \tag{4.75}$$

If the spin state $|\chi\rangle$ lies along $\hat{n}$ ie from Eq.4.61b

$$|\chi\rangle = \begin{bmatrix} \cos\left(\frac{\theta}{2}\right) e^{-i\frac{\phi}{2}} \\ \sin\left(\frac{\theta}{2}\right) e^{i\frac{\phi}{2}} \end{bmatrix} \tag{4.76}$$

then,

$$\hat{U}(t)|\chi\rangle = \begin{bmatrix} \cos\left(\frac{\theta}{2}\right) e^{-i\frac{\omega_0 t + \phi}{2}} \\ \sin\left(\frac{\theta}{2}\right) e^{i\frac{\omega_0 t + \phi}{2}} \end{bmatrix} \tag{4.77}$$

ie we just replaced $\phi \to \phi + \omega_0 t$. In other words, the spin vector corresponding to $|\chi\rangle$ just precesses (rotates) about the z axis, maintaining a constant inclination of θ to the z axis.

For NMR/MRI applications, the spins are exposed to a strong field along z and a weaker magnetic field B_1 rotating in the $x - y$ plane:

$$\hat{H} = -\mu B_z \frac{\hbar}{2}\sigma_z - \mu B_1 \frac{\hbar}{2}(\sigma_x \cos\omega t + \sigma_y \sin\omega t) \tag{4.78}$$

Let $-\mu B_z = \omega_0$ and $g = -\mu B_1/2$, with $B_z \gg B_1$. NB: compare with the Hamiltonian we looked at in Q1 of Homework 2.

The TDSE $i\hbar\frac{\partial\chi}{\partial t} = \hat{H}\chi$ becomes:

$$i\frac{\partial\chi}{\partial t} = \left[\frac{\omega_0}{2}\sigma_z + g(\sigma_x \cos\omega t + \sigma_y \sin\omega t)\right]\chi \tag{4.79}$$

One can write the quantum state in a "rotating frame":

$$\chi(t) = e^{i\frac{\omega t}{2}\sigma_z}\phi(t) \tag{4.80}$$

Substituting in the TDSE:

$$\frac{\omega}{2}\sigma_z e^{-i\frac{\omega t}{2}\sigma_z}\phi + ie^{-i\frac{\omega t}{2}\sigma_z}\frac{\partial\phi}{\partial t} = \hat{H}e^{-i\frac{\omega t}{2}\sigma_z}\phi \tag{4.81}$$

Now multiply both sides by $e^{+i\frac{\omega t}{2}\sigma_z}$

Note that:

$$\sigma_z = e^{+ia\sigma_z}\sigma_z e^{-ia\sigma_z} \tag{4.82}$$

for any a (all these operators commute).

$$i\frac{\partial\phi}{\partial t} = \left[e^{+i\frac{\omega t}{2}\sigma_z}\hat{H}e^{-i\frac{\omega t}{2}\sigma_z} - \frac{\omega}{2}\sigma_z\right]\phi \tag{4.83}$$

But,

$$e^{+ia\sigma_z}(\sigma_x \cos\omega t + \sigma_y \sin\omega t)e^{-ia\sigma_z} = \sigma_x \tag{4.84}$$

(to be proved as an exercise/homework: use I3.d)

Hence, using Eqs.4.82 and 4.84 in Eq.4.83, we see that:

$$i\frac{\partial\phi}{\partial t} = \left[\frac{\omega_0 - \omega}{2}\sigma_z + g\sigma_x\right]\phi(t) \tag{4.85}$$

Thus

$$\phi(t) = e^{-i\left[\frac{\omega_0-\omega}{2}\sigma_z + g\sigma_x\right]t}\ \phi(t=0) \tag{4.86}$$

So we have a time-evolution operator (in the rotating frame):

$$\hat{U} = e^{-i\left[\frac{\omega_0-\omega}{2}\sigma_z + g\sigma_x\right]t} \tag{4.87}$$

Takes the form corresponding to a *time-independent* Hamiltonian, despite the form taken by Eq.4.78.

If we set $\omega_0 \approx \omega$, we have the "resonance" in NMR or MRI.

Then, we have an effective Hamiltonian

$$\hat{H}_{eff} \approx g\sigma_x \tag{4.88}$$

In effect, the strong field along the z-axis has no effect. Despite the fact that $B_z \gg B_1$, only B_1 contributes to the effective Hamiltonian (in the rotating frame).

If $gt = \pi/4$, Eq.4.88 shows that

$$\hat{U} = R_{\pi/2} = e^{-i\frac{\pi}{4}\sigma_x} \tag{4.89}$$

represents a rotation about the x axis by an angle $\pi/2$. ie a spin initially aligned along z is rotated by 90^0 onto the $x-y$ plane. The gradual decay back onto the z axis is characterised by a timescale T_1 and produces a signal which may be detected. The value of T_1 depends on the local environment; the loss of magnetisation in the $x-y$ plane gives another decay timescale T_2. These two timescales form the basis of MRI. If we wanted to calculate the effect of the environment, we would have to go beyond the Schrodinger equation.

But an ingenious technique called "refocussing" removes some of the dephasing effects of the environment. NMR/MRI involves many spins. Spins which have been rotated into the $x-y$ plane according to Eq.4.92, precess about the z axis at slightly different rates because each spin experiences a slightly different B_z (depending on the local environment).

For the $n-th$ spin,

$$\chi_n(t) = e^{-i\beta_n \sigma_z t}\chi_n(t=0) \tag{4.90}$$

where β_n represents the effect of the local magnetic field;it is a constant for each spin but varies from spin to spin..

However, applying a pair of π pulses eliminates this source of error. ie

$$\hat{U} = R_\pi = e^{-i\frac{\pi}{2}\sigma_x} \tag{4.91}$$

we can show:

$$\hat{U}(t) = R_\pi e^{-i\beta_n\sigma_z t} R_\pi = e^{+i\beta_n\sigma_z t} \tag{4.92}$$

We will show this as an exercise in HW4. Use the anticommutation property of different spins (Eq.4.43) ie $\{\sigma_i, \sigma_j\} = 0$.

In effect, sandwiching $e^{-i\beta_n\sigma_z t}$ between two π pulses is equivalent to reversing time $t \to -t$.

Hence, allowing the spin to precess for a further time t

$$R_\pi e^{-i\beta_n\sigma_z t} R_\pi e^{-i\beta_n\sigma_z t} = I \tag{4.93}$$

recovers the identity for all values of β_n. The result is a strong signal called "spin echo" which is also important in MRI.

EXERCISES: "cross-over questions"

This course breaks up into 5 separate sections. Real life is seldom so compartmentalised, so at this stage, we test whether we can apply our knowledge of Sections 1, 2 and 3 to the Sec 4 problems involving spin.

1. The Stern-Gerlach experiment was used to demonstrate the existence of spin. A beam of hydrogen atoms for which $S = 1/2$ so $S_z = \pm 1/2$, enters a magnetic with a field which varies with position z. A potential $V(z) = H_0 z S_z$ is experienced. Write down an estimate for $\psi_{\pm 1/2}(z)$ (ie for both the spin-up and spin-down electrons) using WKB theory (Sec.3), stating all assumptions.

2. A spin 1/2 particle is initially aligned along the z axis. It experiences a Hamiltonian $\hat{H} = -\mu B_z \frac{\hbar}{2} \sigma_z - \mu B_1 \frac{\hbar}{2} (\sigma_x \cos \omega t + \sigma_y \sin \omega t)$ where B_1 is small. Using time dependent perturbation theory, calculate the probability that the spin will be reversed ie spin-down, at time t. You may wish to use Q1 of HW2.

3. A pair of spins interact with each other and are exposed to a time-dependent magnetic field $B_z(t)$ along z. The Hamiltonian $\hat{H} = -\mu B_z(t) \frac{\hbar}{2} (\sigma_{1z} + \sigma_{2z}) + C \sigma_1 \cdot \sigma_2$ where $1, 2$ subscripts refer to spin 1 and spin 2. The two components of the Hamiltonian do not commute, ie $\hat{H} = \hat{A} + \hat{B}$ where $[\hat{A}, \hat{B}] \neq 0$. Write down the form of $T(t + \delta t, t)$ using a split-operator (Suzuki-Trotter) decomposition with errors of order $O((\delta t)^3)$.