Chem 542

Homework for Part 4: Density matrices

1. Density matrices and the Heisenberg equation of motion are often used in derivations and manipulations, but no explicit matrix tends to show up! To remedy this, and provide some practice with manipulations of the density matrix, consider the following two-level system (similar to the TLS discussed in lecture, but without a coupled HO).

A spin Hamiltonian is equal to $\mathcal{H} = s_z$; for spin 1/2, the Hilbert space is spanned by only two orthogonal eigenfunctions, $|s_z = 1/2\rangle$ and $|s_z = -1/2\rangle$, which we'll abbreviate $|1/2\rangle$ and $|-1/2\rangle$. They are eigenfunctions of $\mathcal{H}$ such that $\mathcal{H}\ |1/2\rangle = 1/2\ |1/2\rangle$ and $\mathcal{H}|-1/2\rangle = -1/2\ |-1/2\rangle$. (Let $\hbar = 1$ in the following.)

a. Write down the Hamiltonian matrix in this basis.

b. Write down the density matrix $\rho_S(t)$ corresponding to the initial state $|1/2\rangle$, both in ket-bra and explicit matrix form.

c. Consider the initial state $|a\rangle = (|1/2\rangle + i\,|-1/2\rangle)/\sqrt{2}$ at time t=0; it is clearly not an eigenstate of
$\mathcal{H}$, so the density matrix will be less trivial than in b. Write down $|a(t)\rangle$, then write down its $\rho_S(t)$, in ket-bra and explicit matrix form.

d. Verify that $\rho_S(t)$ satifies the Liouville equation, by comparing the commutator in 3-9 to your result in c.

e. Using $\rho_S(t)$ and the trace operation, compute the expectation values of s_z and s_z^2 as a function of time.

f. Consider a new operator s_x, which could be interpreted as the x component of spin, rather than the z component. Its matrix elements are defined by $\langle 1/2|s_x|-1/2\rangle = 1/2$ and $\langle -1/2|s_x|1/2\rangle = 1/2$, the diagonal elements being zero. What is its expectation value of s_x as a function of time using the density matrices in b. and c.?

g. How would you explain all of this in terms of classical rotating spins? (As best as possible, given this is a quantum system!)