Bohr Frequencies

Suppose H has N e-vecs $|E_n\rangle$

$$H|E_n\rangle = E_n|E_n\rangle$$

all different. Then $I = \sum_{n=1}^{N} |E_n\rangle\langle E_n|$.

Also

$$U(t)|E_n\rangle = e^{-\frac{iHt}{\hbar}}|E_n\rangle = e^{-iE_nt/\hbar}|E_n\rangle$$

and so the mean value of any operator A in the state $|E_n\rangle$ will vary as

$$\langle E_n|U^\dagger(t)\,A\,U(t)|E_n\rangle = e^{\frac{iE_nt}{\hbar}}\langle E_n|A|E_n\rangle e^{-\frac{iE_nt}{\hbar}}$$

$$= \langle E_n|A|E_n\rangle$$

which is to say, not at all. It is constant in time. That's why e-vecs of H are called stationary states.

An arbitrary state $|\psi\rangle$ can be expanded as

$$|\psi\rangle = I|\psi\rangle = \sum_{n=1}^{N} |E_n\rangle\langle E_n|\psi\rangle .$$

So the mean value of any operator A will in the state $|\psi\rangle$ will evolve as

$$\langle\psi|U^\dagger(t)\,A\,U(t)|\psi\rangle = \sum_{m=1}^{N}\sum_{n=1}^{N} \langle\psi|E_m\rangle\langle E_m|A|E_n\rangle\langle E_n|\psi\rangle \, e^{i(E_m-E_n)t/\hbar} .$$

The frequencies

$$\omega_{mn} = \frac{(E_m - E_n)}{\hbar}$$

are the Bohr frequencies. The time dependence of every operator is a linear combination of terms

$$e^{i(E_m - E_n)t/\hbar} = e^{i\omega_{mn}t}$$

with coefficients $\langle \psi | E_m \rangle \langle E_m | A | E_n \rangle \langle E_n | \psi \rangle$.

If A is compatible with H, that is, if

$$[A, H] = 0, \qquad \text{(comp)}$$

then A and H are simultaneously diagonalizable. Equivalently, Eq. (comp) implies

$$0 = \langle E_m | [A, H] | E_n \rangle = (E_n - E_m) \langle E_m | A | E_n \rangle.$$

Thus the mean value of any operator that commutes with H in an arbitrary state is

$$\langle \psi | U^\dagger(t) A U(t) | \psi \rangle = \sum_{n=1}^{N} \langle \psi | E_n \rangle \langle E_n | A | E_n \rangle \langle E_n | \psi \rangle$$

only involves the diagonal matrix elements $\langle E_n | A | E_n \rangle$ and so has no time dependence due to $U(t)$. Of course, if A explicitly depends on t, then so does $\langle \psi | U^\dagger(t) A U(t) | \psi \rangle$.