Spring 2015 Cume Problem #3: Two-state interaction problem with identical molecules

(a) Base Hamiltonian before interaction potential:

Since site energies are equal, Ea = Eb =

Given the orthonormality of the states,

With an analogous solution for

Introduce the interaction potential to Hamiltonian

Set , simplifying H to

But are no longer eigenstates of H with Vdd incorporated.

Changing basis to,

(b) We see that

And

So, and are eigenstates of the new Hamiltonian with eigenvalues of Vdd and –Vdd, respectively.

(c) Given we need to determine whether the states are light or dark for H- and J-aggregate cases. Thus, if , then we have light states.

For J-aggregate transition dipoles, where µa = µb=µ,

And

The J-aggregate states each have a nonzero transition dipole moment equaling µ=µa=µb, making them allowed transitions (light states).

For the H-aggregate case, µa = -µb

And

Thus for an H-aggregate, both states are dark.

(d) Starting toward the goal of determining tunneling rates, we construct a general time-dependent (non-stationary) state expression given an arbitrary stationary state . We can express it using the basis by a superposition of identities of the individual states, given generally as

Inserting the identity with our base kets and acting on , we get

Given the solution to the time-dependent Schrödinger equation for an arbitrary state

We get

(e) To start the tunneling problem, we express the state using

First, solve the inner products and

Thus

(f) For our tunneling problem, we move from site a at t = 0 to site b at some later time t. We accomplish this by first determining the probability amplitude A(t)

Evaluating the inner products and we get

Plugging this into A(t) we get

We set and use Euler’s relations and to get

Squaring the probability amplitude yields the probability of transfer from a to b

(g) The tunneling (transfer) rate constant is proportional to the oscillation frequency