Homework assignment 4

Problem 1:   Coupling of two angular momenta

Consider a system described by two angular momenta, $S_1 = 1$ and $S_2 = \frac{1}{2}$. (This could be the orbital angular momentum and spin of an electron in $2p$ state, or it could represent a deuterium atom where S_1 is the spin of the nucleus and S_2 is the spin of the electron).

(a) Write down the direct product basis vectors for the system, $|m_1\ m_2 >$.

Assume now that the two angular momenta are coupled in such a way that an extra term, W, is introduced in the Hamiltonian:

$$W \ = \ a\ \vec{S}_1 \cdot \vec{S}_2.$$

(This could be spin orbit coupling in the case of the 2p electron, or a part of the hyperfine splitting of the deuterium atom).

(b) Write an expression for the time derivative of the expectation value $< S_{1x} >$ in terms of the vectors $\vec{S}_1$ and $\vec{S}_2$ and the coupling constant a.

(c) Write down the eigenvectors for the total angular momentum

$$\vec{J} \ = \ \vec{S}_1 \ + \ \vec{S}_2$$

in terms of the direct product basis. (You can get the relevant Clebsch-Gordan coefficients from the web at, for example, Wikipedia)

(d) What are the energy levels of the system and what is their degeneracy?

(e) Assume that at time $t = 0$ the two angular momentum vectors are aligned in the opposite direction, $m_1 = -1$ and $m_2 = \frac{1}{2}$. Give an expression (in terms of a) for the state vector after time t. Would it be possible to find some time t_r at which the two spins have reversed completely, i.e. $m_1 = 1$ and $m_2 = -\frac{1}{2}$ (as could be done in the case of two spin $\frac{1}{2}$ particles)? Explain.

Problem 2:   Transition state theory and the harmonic approximation

(i) Describe how a variational principle can be derived for the selection of the optimal transition state dividing surface and explain how corrections to the transition

state theory approximation to the rate constant can be obtained from classical trajectories.

(ii) A Li atom on the (100) surface of an iron crystal can diffuse over the surface by thermally activated hops between adjacent sites. The atom can be considered to be a particle moving on a periodic, three-dimensional potential energy surface (PES) while the iron atoms are fixed. This is a good approximation since the Li atom is so much lighter than the iron atoms.

The PES can be approximated as

$$V(x, y, z) = V_s \left(e^{-sin(2\pi x/b) - sin(2\pi y/b) - 2\alpha z} - 2e^{-\alpha z} \right).$$

One of the minima is at $(x, y, z) = (b/4, b/4, -2/\alpha)$ and one of the adjacent saddle points is at $(x, y, z) = (b/4, 3b/4, 0)$.

A reasonable approximation is to set $\alpha = 2.0$ Å^{-1}. Then, a second order Taylor expansion of the PES around the minimum is

$$V(x, y, z) = V_s e^2 \left(-1 + 2 \left(\frac{\pi}{b} \right)^2 \left(\left(x - \frac{b}{4} \right)^2 + \left(y - \frac{b}{4} \right)^2 \right) + 4(z + 1)^2 \right)$$

and a similar expansion around the saddle point is

$$V(x, y, z) = V_s \left(-1 + 2 \left(\frac{\pi}{b} \right)^2 \left(\left(x - \frac{b}{4} \right)^2 - \left(y - \frac{3b}{4} \right)^2 \right) + 4z^2 \right).$$

Write down an expression for the rate constant as a function of temperature using the harmonic approximation to TST. Then use the values $V_s = 0.1$ eV and $b = 2.87$Å to simplify the expression as much as possible. Note that $\sqrt{eV/amu}/$Å$= 1.0 \times 10^{14}$ s^{-1}.

(iii) How long is the time period on average between diffusion hops at room temperature, at 400 K and at 500 K?

(iv) Rewrite the HTST expression for the rate constant to take into account some of the quantum mechanical effects. Do this by introducing the classical partition function for the harmonic oscillator of each one of the vibrational modes, $q_i = k_B T / \nu_i$ in the HTST expression for the rate constant instead of the vibrational frequency, ν_i. Then, replace the classical partition function of each mode with the corresponding quantum mechanical partition function. Evaluate the hopping rate using this 'quasi-quantum' approximation at room temperature and compare with the rate constant obtained with classical HTS in part (iii). Discuss to what extent quantum effects have been included with this quantum mechanical generalization of the rate constant expression and identify possible quantum mechanical effects that still have not been taken into account.