Midterm – CH125A

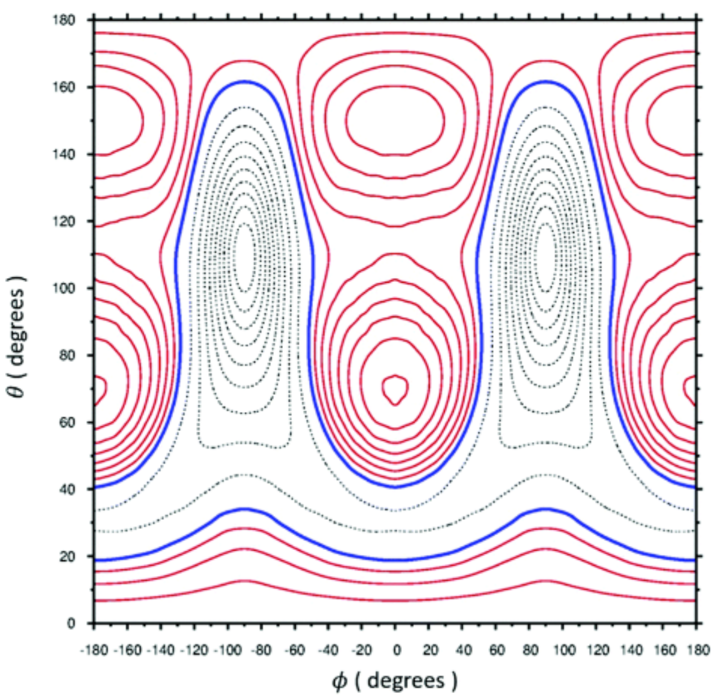
This is open notes, open book, open internet. No collaboration is allowed.

(25 Points) Problem 1: Please reply to the following with a sentence or few sentence answer.

A. What higher lying principle is the Hamiltonian derived from that was not used in Newton's formulation?
B. Why is the result of a simple harmonic oscillator (SHO) applicable to so many cases across science?
C. What do the on and off diagonal components of a matrix operator correspond to?
D. Label each term in Schrodinger's equation with its meaning or intuitive importance.

(15 Points) Problem 2: The following potential energy surfaces corresponds to an ozone-Ar complex. The symmetry of the potential energy surface mirrors that of ozone. Red is positive energy while black is negative. In coordinates of (θ,φ), please answer the following:

A. If the molecule started at (θ=70,φ=0) where would it relax to and with what probability?
B. Transition states are typically identified as a "saddle point" on the potential energy plot. Give the coordinate of the saddle point between the two potential minima you found in part A.



https://doi.org/10.1039/C9CP01044K

(15 Points) Problem 3: An operator *R* acts in a space of three orthonormal states, $|T\rangle, |U\rangle, |V\rangle$ and is represented as outer products as $R = 2|T\rangle\langle T| + 5|U\rangle\langle U| - 5|V\rangle\langle V|$. These three states can be expressed as linear combinations of three other orthonormal states $|1\rangle, |2\rangle, |3\rangle$ as follows

$$|T\rangle = |1\rangle; \qquad |U\rangle = |2\rangle\frac{1}{\sqrt{2}} + |3\rangle\frac{e^{-i\phi}}{\sqrt{2}}; \qquad |V\rangle = |2\rangle\frac{e^{i\phi}}{\sqrt{2}} - |3\rangle\frac{1}{\sqrt{2}}$$

Express *R* as a sum of the outer products in the form

$$R = \sum_i \sum_j |i\rangle c_{ij} \langle j|$$

(20 points) Problem 4:

A. What number does $|X\rangle$ need to be in order for the following to not be zero? What is the expectation value with this $|X\rangle$?

$$\langle X|a(a^\dagger)^3 a|n\rangle$$

B. Prove, using commutator relations, that $\langle 1|1\rangle$ is orthonormal for the states of the SHO. Hint, use $a^\dagger|0\rangle$ and the commutator for $[a, a^\dagger]$.

(25 Points) Problem 5: In this problem, we apply Fermi's golden rule to a 3-level system. The energies of our states are:

$$H|0\rangle = (400\ cm^{-1})|0\rangle$$

$$H|1\rangle = (1600\ cm^{-1})|1\rangle$$

$$H|2\rangle = (3400\ cm^{-1})|2\rangle$$

We'll assume that our particle starts in the ground state ($|0\rangle$) and any wavefunction in this system can be described as a linear combination of these states.

A. Recall that Fermi's golden rule allows us to calculate any transition rate (in s^{-1}) as:

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar}\sum_f \left|\langle f|V_{fi}|i\rangle\right|^2 \delta(E_f - E_i - \hbar\omega)$$

What does each part of Fermi's golden rule mean conceptually?

B. What photon energies (in cm^{-1}) can excite optical transitions in this system?

C. For this system, we assume that only optical transitions occur. The nonzero optical transition matrix elements are:

$$\langle 1|V_{fi}|0\rangle = \langle 0|V_{fi}|1\rangle = 5 \cdot 10^{-12}\sqrt{J}$$
$$\langle 2|V_{fi}|0\rangle = \langle 0|V_{fi}|2\rangle = 3 \cdot 10^{-12}\sqrt{J}$$
$$\langle 2|V_{fi}|1\rangle = \langle 1|V_{fi}|2\rangle = 6 \cdot 10^{-12}\sqrt{J}$$

Define your basis vectors ($|0\rangle$, $|1\rangle$, and $|2\rangle$) and write the full 3x3 transition matrix (V_{fi}) in matrix notation.

D. For our purposes, we will assume that $\delta(0) = 1$ for photons that are on-resonance with an optical transition. The absorption rate thus simplifies to:

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar}\sum_{f}\left|\langle f|V_{fi}|i\rangle\right|^2$$

Calculate the absorption rate for photons with energy $\hbar\omega$ = 3000 cm^{-1}. (Recall that $\hbar$ = 1.05·10^{-34} J·s.)

5 Bonus points: What homework or test problem so far was your least favorite?