

Problem Set PS03

ISSUED: 1/20/99 Due: 1/27/00

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Name _____

Instructions. Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

Exercises

1. Verify that the ‘left’ and ‘right’ states of a two level system are not eigenfunctions of the two level Hamiltonian unless the two levels are degenerate. That is, these states are not solutions of the *time independent* Schrödinger equation.
2. Now verify that the ‘left’ and ‘right’ states of a two level system are solutions of the *time dependent* Schrödinger equation.
3. The Bohr frequency of a two level system is defined as $\omega_0 = \frac{E_2 - E_1}{\hbar}$. Write the final result of Eq. (11.116) in terms of the Bohr frequency (simplify as best you can). Does it make sense to say that the Bohr frequency gives the frequency with which a system oscillates from the ‘left’ to ‘right’ states.
4. A superposition of a two level system is prepared in the ‘left’ state at time zero. The probability of finding the system in state 1 at time t is given by $|\int \Psi_L^*(t=0)\Psi_1(t)d\Omega|^2$. Evaluate this probability and comment on its time dependence. Why can the probability of finding the system in state 1 never be one or zero?
5. Look at Table 1 of A. Amann “Structure, dynamics and spectroscopy of single molecules: A challenge to quantum mechanics” *J. Math. Chem.* **18**, 247 (1995).
 - (a) What is the Bohr frequency in s^{-1} for the molecules listed in the table?
 - (b) The ammonia inversion was actually the first system ever used to produce a laser beam. Actually at the time it was called a maser. Based in the level splitting for the ground and first excited states of ammonia, what do you think the “m” in maser stands for?
 - (c) How many years would you expect to wait before aspartic acids changes its chirality? (The age of the universe is 10^{15} s.)
6. Use perturbation theory to find the first order approximation to the ground state energy for a sextet oscillator ($V(x) = \frac{1}{2}kx^2 + \lambda x^6$).
7. Use variational theory to estimate the ground state energy for a special quartic oscillator having potential

$$V(x) = x^4.$$

Use

$$\psi(x) = e^{-px^2}$$

as your trial wavefunction. Your algebraic equation for p will have several roots you will need to choose the correct one. Also make a plot of the optimized ground state wavefunction and $V(x)$. (For convenience set $\frac{\hbar^2}{2m}$ to one.)

Conceptual Problems

8. How does the Bohr frequency change with the energy gap in a two level system? Is this consistent with the first Exercise above?
9. A superposition of the 2s and 2p_z orbitals of helium is prepared using a laser pulse. Treat the 2s and 2p_z as a two level system and draw a qualitative picture of the superposition state as it evolves in time.
10. The resonance stabilization energy for benzene is 36Kcal/mol. What is the two level system energy gap (in wavenumbers)? Speaking classically how fast does benzene oscillate from one resonance structure to the other? Remember the electrons are not really moving when they are in a state described by an eigenfunction.
11. Consider each of the following systems. If you were to attack the problem using perturbation theory what model would you chose as the solvable system. Also state what the perturbative part of the Hamiltonian would account for.
 - (a) The π electrons of a bucky ball in an external magnetic field
 - (b) The quantum Kepler problem (a particle orbiting a center where the orbits are elliptical)
 - (c) A square quantum dot.
 - (d) The quantum weeble
 - (e) Helium
 - (f) Particle on an egg.

Computer Problems

12. Construct a quantum rattle by making a 'left' superposition of the first two states of a particle in a box. Print out an array graphics which shows the mod-square of the wavefunction as for various times. Be sure to show at least a few cycles.
13. Compare the time evolution of a Gaussian wavepacket (coefficients: $e^{-0.01n^2}$) prepared with particle in a box wavefunctions versus that prepared with harmonic oscillator wavefunctions. For simplicity use $\varphi_n = e^{in^2t} \sin n\pi x$ for the particle in a box wavefunctions and $\varphi_n = e^{i(n+\frac{1}{2})t} \frac{1}{\sqrt{2^n n!}} H_n(x) e^{-\frac{x^2}{2}}$ for the harmonic oscillator wavefunctions. Sum the first 20 terms in the superposition. (Note your time units will not correspond to seconds.) Describe what happens to each of the wavepackets as they evolve in time.

① $\psi_2 = \frac{1}{\sqrt{2}}\psi_1 + \frac{1}{\sqrt{2}}\psi_2$ $\psi_2 = \frac{1}{\sqrt{2}}\psi_1 - \frac{1}{\sqrt{2}}\psi_2$

$H\psi_2 = (E_1 S_{10} + E_2 S_{20}) (\frac{1}{\sqrt{2}}\psi_1 + \frac{1}{\sqrt{2}}\psi_2)$

$= \frac{E_1}{\sqrt{2}}\psi_1 + \frac{E_2}{\sqrt{2}}\psi_2$ not eigenfunctions unless $E_1 = E_2$

② $\psi_2 = \frac{1}{\sqrt{2}}\psi_1 e^{-\frac{i}{\hbar}E_1 t} + \frac{1}{\sqrt{2}}\psi_2 e^{-\frac{i}{\hbar}E_2 t}$

$i\hbar \frac{\partial \psi_2}{\partial t} = (E_1 S_{10} + E_2 S_{20}) \psi_2$

$i\hbar \frac{\partial}{\partial t} (\frac{1}{\sqrt{2}}\psi_1 e^{-\frac{i}{\hbar}E_1 t} + \frac{1}{\sqrt{2}}\psi_2 e^{-\frac{i}{\hbar}E_2 t}) = \frac{E_1}{\sqrt{2}}\psi_1 e^{-\frac{i}{\hbar}E_1 t} + \frac{E_2}{\sqrt{2}}\psi_2 e^{-\frac{i}{\hbar}E_2 t}$

$\frac{1}{\sqrt{2}} \frac{\partial}{\partial t} \psi_1 e^{-\frac{i}{\hbar}E_1 t} + \frac{1}{\sqrt{2}} \frac{\partial}{\partial t} \psi_2 e^{-\frac{i}{\hbar}E_2 t} = \frac{E_1}{\sqrt{2}} \psi_1 e^{-\frac{i}{\hbar}E_1 t} + \frac{E_2}{\sqrt{2}} \psi_2 e^{-\frac{i}{\hbar}E_2 t}$

$\frac{1}{\sqrt{2}} \psi_1 e^{-\frac{i}{\hbar}E_1 t} \pm \frac{1}{\sqrt{2}} \psi_2 e^{-\frac{i}{\hbar}E_2 t} = \frac{E_1}{\sqrt{2}} \psi_1 e^{-\frac{i}{\hbar}E_1 t} \pm \frac{E_2}{\sqrt{2}} \psi_2 e^{-\frac{i}{\hbar}E_2 t}$

③ $|\int \psi^*(x,t) \psi(x,t) dx|^2 = \frac{1}{2} (1 + \cos \frac{E_1 - E_2}{\hbar} t)$

$= \frac{1}{2} (1 + \cos(\omega_0 t))$ but $\cos(a) = \cos a$

$= \frac{1}{2} (1 + \cos \omega_0 t)$

$\psi_0 = \frac{1}{\sqrt{2}} e^{-\frac{1}{2} \frac{\lambda \pi}{a} x^2}$

⑥ $E_0^{(1)} = \int \psi_0^* \lambda x^6 \psi_0 dx$

$= \frac{\lambda}{\pi} \int_0^\infty x^6 e^{-\sqrt{\frac{2m}{\hbar^2}} x^2} dx$ $\frac{15 \lambda}{8 (\frac{2m}{\hbar^2})^{3/4} \sqrt{\pi}}$

$E_0 \approx E_0^{(0)} + E_0^{(1)} = \hbar \omega (n + \frac{1}{2}) + \frac{15 \lambda}{8 (\frac{2m}{\hbar^2})^{3/4} \sqrt{\pi}}$

⑦ $E_{trial} = \frac{\int \psi_{trial}^* H \psi_{trial} dx}{\int \psi_{trial}^* \psi_{trial} dx} = \frac{\int_0^\infty e^{-px^2} (\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + x^4) e^{-px^2} dx}{\int_0^\infty e^{-2px^2} dx}$

$E_{trial} = \frac{\frac{\hbar^2}{2m} \int_0^\infty e^{-px^2} \frac{d^2}{dx^2} e^{-px^2} dx + \int_0^\infty x^4 e^{-2px^2} dx}{\int_0^\infty e^{-2px^2} dx}$

$E_{trial} = \frac{(3m + 16p^3)\sqrt{\pi}}{16p^2} = \frac{3m + 16p^3}{16p^2}$

$\frac{\partial E_{trial}}{\partial p} = \frac{-3 + 8p^3}{8p^2} = 0 \Rightarrow$ This eqn has 3 roots only one is real $p = (\frac{3}{8})^{1/3}$

$\psi = e^{-\frac{(\frac{3}{8})^{1/3}}{2} x^2}$

④ $|\int \psi_2^*(0) \psi_1(x) dx|^2 = |\int (\frac{1}{\sqrt{2}}\psi_1^* + \frac{1}{\sqrt{2}}\psi_2^*) (\psi_1 e^{-iE_1 t}) dx|^2$

$= |\frac{1}{\sqrt{2}} e^{-iE_1 t} \int \psi_1^* \psi_1 dx + \frac{1}{\sqrt{2}} e^{-iE_2 t} \int \psi_1^* \psi_2 dx|^2$

$= |\frac{1}{\sqrt{2}} e^{-iE_1 t} / 2 = \frac{1}{2}$

The probability of finding the system in state 1 is 50% for all time.

If we were to measure the energy we must get one of the eigenvalues, E_1 or E_2 . Each of these have a 50% chance of resulting.

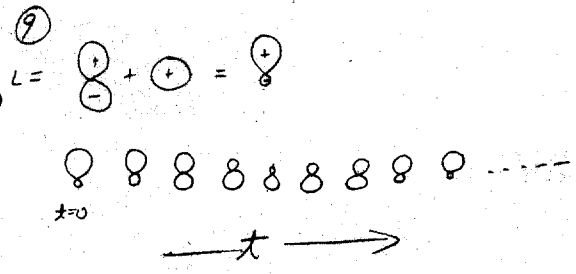
⑤ a

molecule	ω_0
mda	1.6×10^{12} Hz
Ammonia	2.55×10^9 Hz
Hap.	5.49×10^7 Hz
AA	3.0×10^{-51} Hz

b From a the Bohr frequency \Rightarrow 50 "M" stands for microwave is 2.55×10^9 Hz

c $\frac{1}{2.0 \times 10^{51} \text{ Hz}} = 3.3 \times 10^{50} \text{ s} = 1.0 \times 10^{43} \text{ years}$ over 3 times the age of the universe.

⑧ As the energy gap decreases the Bohr frequency decreases. When the energy levels become degenerate, the Bohr frequency goes to zero. This is consistent with the first exercise. For example if the system is in the 'left' state and the Bohr frequency is zero then it will remain in the 'left' state for all time: hence the left state is an eigenstate.



10 $36 \text{ kcal/mol} = \frac{150 \text{ kJ}}{\text{mol}} \frac{1 \text{ mol}}{6.023 \times 10^{23} \text{ molecules}} = 2.4 \times 10^{-19} \text{ J/molecule}$

$= 12160 \text{ cm}^{-1}$

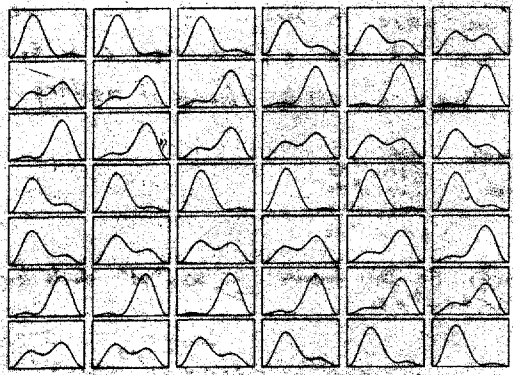
$\Delta E = 24320 \text{ cm}^{-1}$

$\omega_0 = 7.30 \times 10^{14} \text{ Hz}$

- 11
- | | | |
|-----|--|---|
| (a) | Soluble system
particle on a sphere | Perturbation
Electric field |
| (b) | particle on a ring | Elliptical Orbits
rather than circular |
| (c) | 2D particle in a box | None infinite
potential energy |
| (d) | Hydrogen | e-e term |
| (e) | particle on sphere | none spherical
nature of the egg |

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Quantum Rattle



13 The Gaussian wavepacket for the H₂O₂ remains as a wavepacket for all time. The wavepacket for the box disperses with time.